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RESEARCH PROJECT INITIATION

Date: 27 August 1973

Project Title: Collision Induced Optical Spectra of Solids

Project No: G-41-630

Principal Investigator: Dr. E. W. Thomas

Sponsor: National Science Foundation

Agreement Period: From October 1, 1973 Until March 31, 1975

Type Agreement: Grant No. GH-40217

Amount: $29,000 NSF
5,782 GIT (cost-share account G-41-325)
$34,782 TOTAL

Reports Required: Annual Technical Letter
Final report due at termination

Sponsor Contact Person (s): Wilbur W. Bolton, Jr.
National Science Foundation
Washington, D. C. 20550

Assigned to: Physics

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RA-3 (6-71)

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OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Post Ex

Date: January 12, 1978

Project Title: Collision Induced Optical Spectra of Solids

Project No: G-41-630

Project Director: Dr. E. W. Thomas

Sponsor: National Science Foundation

Effective Termination Date: 9/30/77 (Grant Expiration)

Clearance of Accounting Charges: by 9/30/77

Grant/Contract Closeout Actions Remaining: NONE.

Otis - My sheet shows equipment.

_ Final Invoice and Closing Documents
_ Final Fiscal Report
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ion pump - 2055
gas Analyser - 4500

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CA—4 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

28 October 1974

SCHOOL OF PHYSICS

Dr. Richard Silberglitt
Solid State Physics Program
Division of Materials Research
National Science Foundation
Washington, D. C. 20550

Dear Dr. Silberglitt:

This letter is to serve as the "annual letter technical report" as stipulated in NSF publication NSF 73-12.

Name of Institution Georgia Institute of Technology

Name of Principal Investigator Professor Edward W. Thomas

Grant No. GH-40217

Starting Date 1 October 1973

Completion Date 31 March 1975

Grant Title "Collision Induced Optical Spectra of Solids"

Description of Research

In a recent paper[1] I showed, for the first time that ion impact on metals gives rise to a broad band continuum of light emission. Various explanations have been proposed for the mechanism of the emission process and the objective of the work supported by this grant was to determine which of these was correct. The work was envisaged as a two year project. The first year was to be devoted to constructing suitable equipment to perform these studies and to carrying out a general survey of the emissions observed in various ion-surface combinations. The second year's work was to be concerned with a detailed understanding of the mechanism involved and their relationship to established properties of solids. This report covers the first year's work. We are pleased to report that the objectives for the first year have been successfully accomplished and that we are making good progress on the understanding of the emission mechanism.

The experimental arrangement we constructed is essentially that which we discussed in our original proposal and is similar to a system used previously by the writer in another institute[1]. The monoenergetic, mass-analyzed projectile beam is provided by a conventional accelerator facility; all the work performed

1. C. KerkdijK and E. W. Thomas, Physica 63, 577 (1973)

to date has been with a machine operating between 5 and 30 kV but we also have available a 70 to 1,000 kV Van de Graaff accelerator. The targets are mounted on a standard manipulator in a clean, ultra-high-vacuum, chamber ($p < 10^{-9}$ Torr) that is isolated from the poor vacuum of the accelerator, by three stages of differential pumping. A sapphire window in the chamber allows observation of the light emitted from the point where the projectile beam strikes the target. The light emission is analyzed by a conventional 1/2 meter scanning monochromator fitted with a photomultiplier detector. Recording of signals is semi-automated. Considerable attention has been paid to utilizing reproducible target surface conditions; all materials used are of the highest purity that is commercially available and impurity levels are a few p.p.m.. Polycrystalline metal targets, utilized in the form of thin strip, are both mechanically and electrolytically polished. Alkali halides are utilized in the form of polished single crystals. Once the specimens are in place they are further cleaned by sputtering and heating; we find, however, that sputter cleaning does not significantly alter the observations so that the phenomena under investigation are not influenced by thin oxide films. I would note that the vacuum environment for the targets is provided by ion pumping and that the phenomenon known as "ion-burn" is not present on the samples after they have been bombarded. "Ion-burn" is a carbon film caused by decomposition of hydro-carbons and is commonly found on surfaces that have been subjected to intensive ion bombardment; it occurs even for minute hydrocarbon contaminant levels and there is evidence that hydrocarbons actually migrate across a surface to the beam spot. The absence of such burn indicates that hydrocarbons are not present and this is confirmed by analyzing the vacuum environment with a residual gas analyzer. This is important because there is evidence[2] that the carbon film may induce (or catalyze) formation of excited molecules; molecular emissions might conceivably give rise to broad spectral features.

On completion of the apparatus we have performed the survey of collision situations that was proposed. All work has been done so far with projectiles of energies from 5 to 35 KeV; work with higher energies will be performed before the expiry date of this grant. Simply stated we have recorded the spectra induced by impact of all the following projectiles on all the listed target surfaces.

Projectiles: - H^+, He^+, Ar^+

Targets: - Al, Cu, Nb, Fe, Mo, NaCl, NaBr, NaF, KF, SiO_2

A few studies have been performed with H°, H_2^+ and H_3^+ beams but these give the same spectra as H^+. Samples of a few of the observed broad-band spectra are shown in Figs. 1 and 2. In all cases there are weak atomic line emissions from scattered, excited, projectiles and for the impact of heavier ions (Ar^+, and sometimes He^+) there are clear emissions from excited sputtered target

2. V. V. Gritsyna, T. S. Kiyan, A. G. Koval', and Ya. M. Fogel', Zh. E. T. F. Pis. Red. 9, 212 (1969)

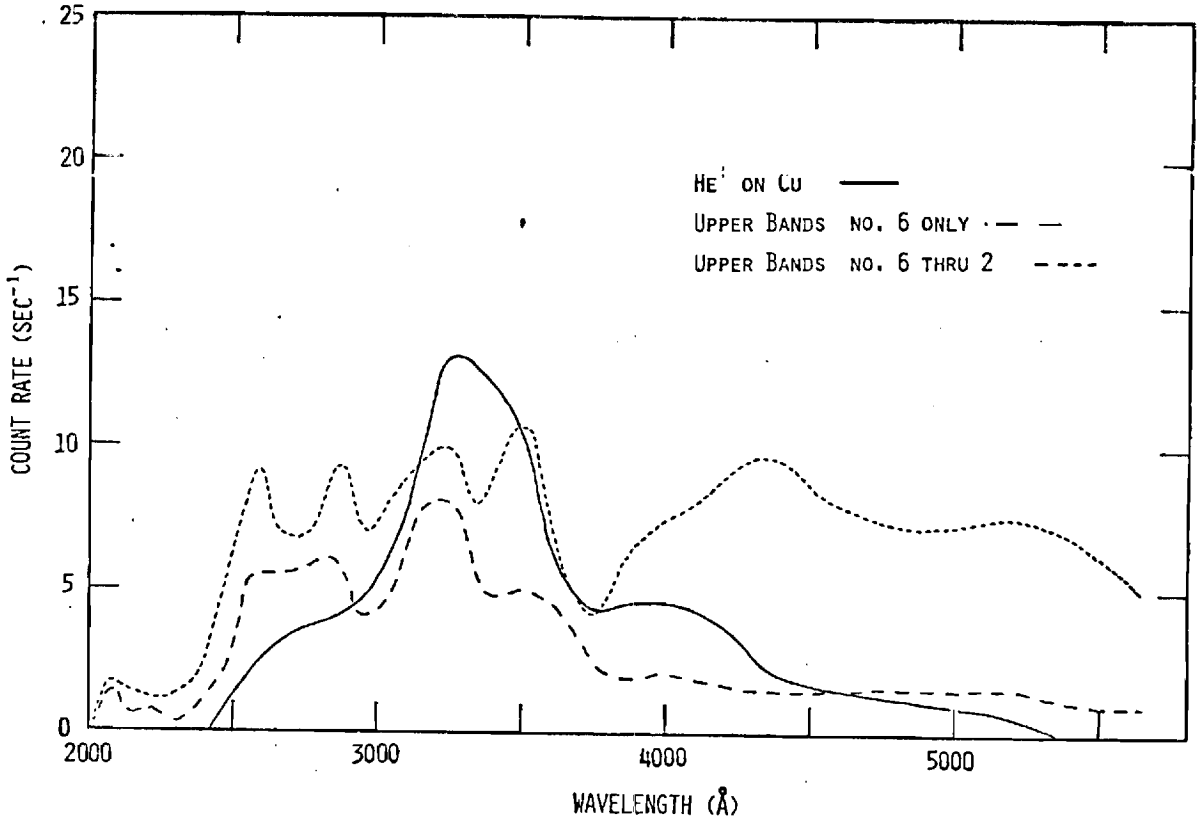

Figure 1a. Emission band observed for 25 KeV He^+ incident on Cu. Broken curves indicate the predicted emission. (See text).

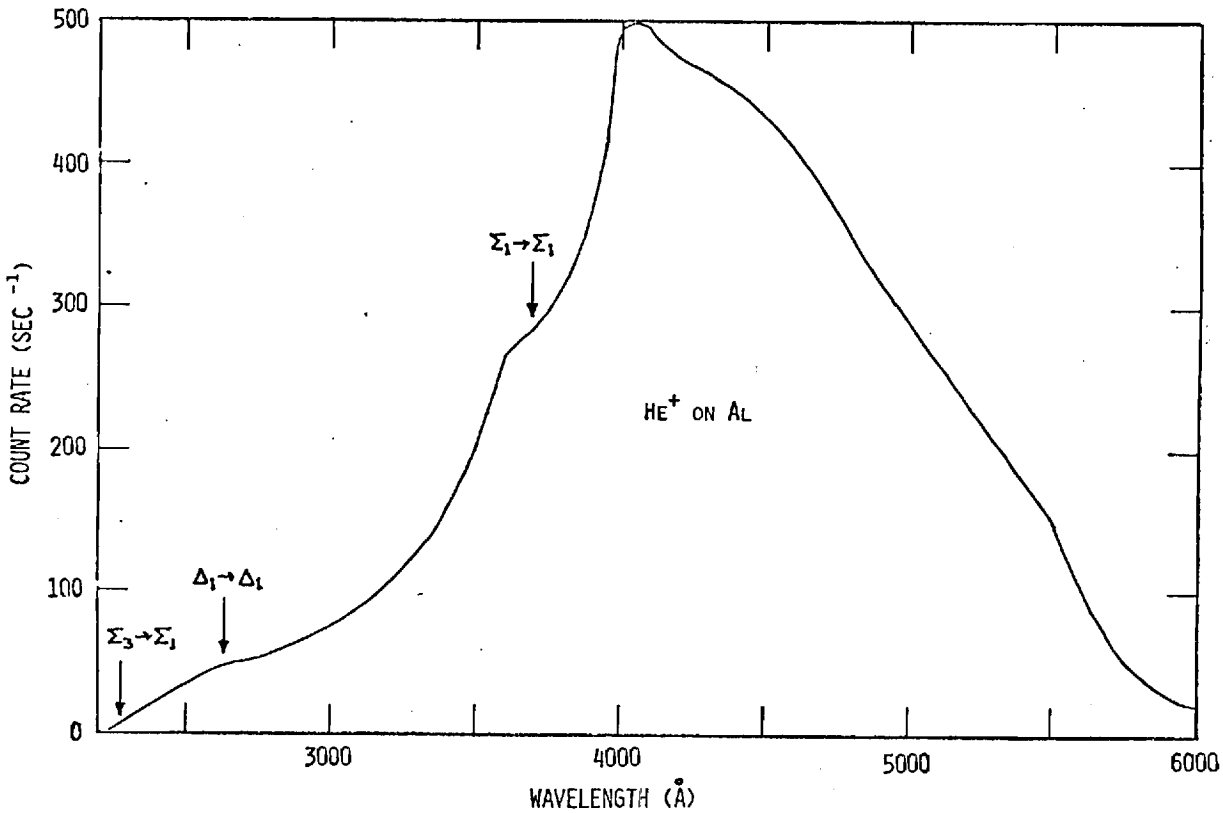

Figure 1b. Emission band observed for 25 KeV He^+ incident on Al.

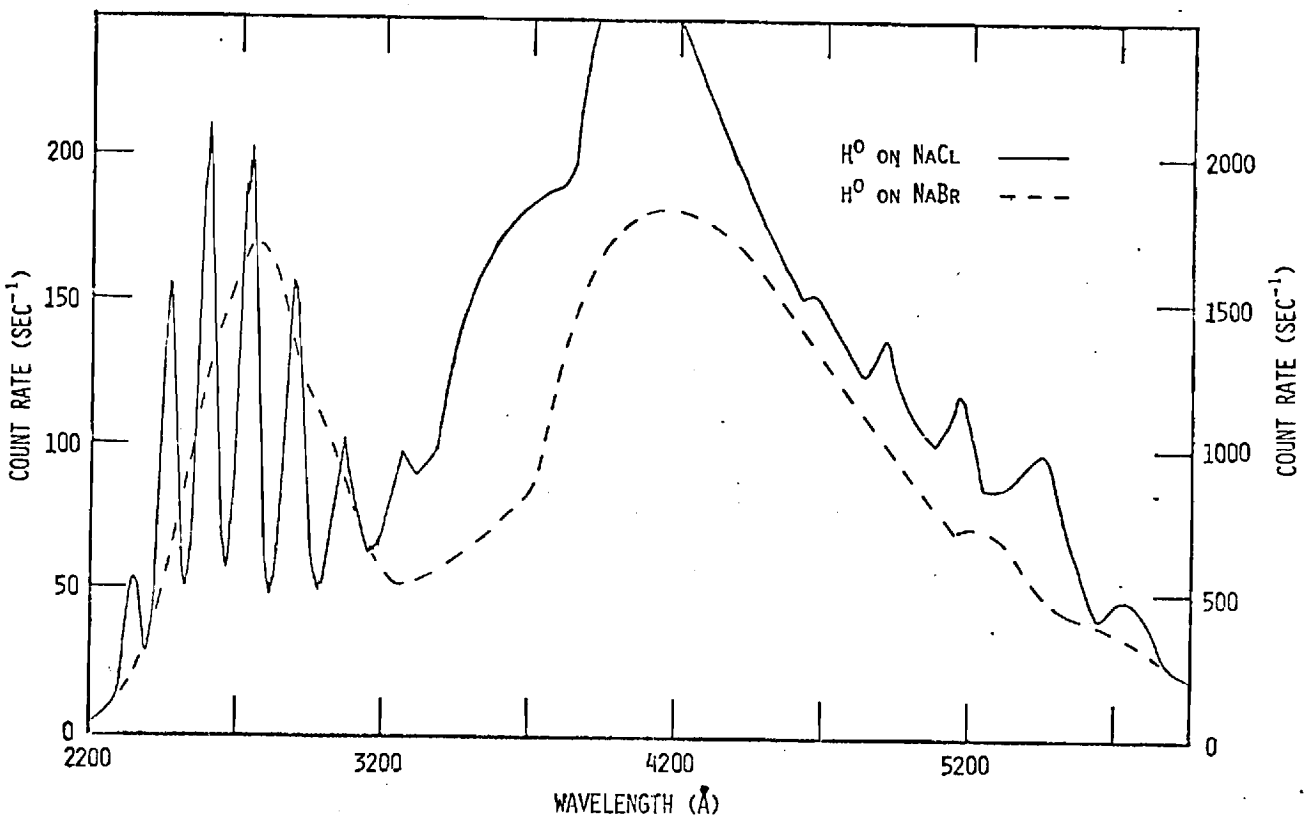

Figure 2. Emission bands observed for 25 KeV H° atoms incident on NaCℓ and NaBr. The count rate scale to the left is for NaCℓ and to the right for NaBr, so the latter is approximately ten times more intense than NaCℓ.

atoms; the figures shown here have had such line emission removed in order to clearly display the bands. He^+ and H^+ ions incident on the metals give a rather weak band emission; Ar^+ ions on the metals give a very rich spectrum of lines from sputtered atoms and the bands are either absent or obscured by the far more intense lines. The observed broad bands for metals have the same spectral form for both H^+ and He^+ impact. In the case of the alkali halides the broad bands are very intense and have the same spectral form for both heavy ion (Ar^+) and light ion (H^+, He^+) impact. In all cases the band intensity increase, with the projectile energy and with increasing angle between the projectile beam and surface normal; the relative shape of the bands do not change.

We have devoted much time to ensuring that the bands are not caused by instrumental problems or contaminant effects. It has been suggested[3] that the bands may be due to fluorescence of the windows through which the observations are made; this has been shown not to be the case in our apparatus. It has also been suggested[4] that emission from the insulating materials is caused by secondary electrons; again in our apparatus this has been shown not to be the case. The sputtering coefficient of the projectile ions is about unity for light ions (H^+ and He^+) and higher for Ar^+; thus any monolayers of contaminant on the surface should be removed in a matter of minutes and thereafter the surface will remain atomically clean while it is under bombardment. We have also tried the effect of deliberately flooding the target chamber with oxygen to a pressure of 10^{-5} Torr; in all cases, except Al targets, the emission remained completely unchanged. For Al bombarded by Ar^+ in an atmosphere of Oxygen at 10^{-5} Torr we do observe some very weak additional bands; these are identical to those reported by G. E. Thomas and E. E. de Kluizenaar[5] and identified as due to Aluminum Oxide.

We have not yet come to a definite conclusion as the origin of all these bands butwe do have some useful interim conclusions for the metals and to a lesser extent for the alkali halides. These will now be discussed separately below. We shall not attempt to discuss in detail the various mechanisms we have rejected but concentrate on those which remain plausible.

(a) Metals

The observed band emissions are thought to be due to electron-hole recombination. The projectile ion excites an electron from the valence band to some vacant level therebye forming a "hole". Subsequently a

3. N. H. Tolk, D. L. Simms, E. B. Foley and C. W. White, Radiation Effects 18, 221 (1973)

4. C. Kerkdijk (Private Communication)

5. G. E. Thomas and E. E. de Kluizenaar, Le Vide 167, 190 (1973).

second electron in a state above the hole decays into it with the emission of a photon.

With a few simplifying assumptions we have predicted the general line shape expected for the recombination process in copper. This is a good case to consider since there are extensive detailed band structure calculations in the literature, particularly those of Burdick[6]. A major assumption is that holes are formed with equal likelihood at all places in the combined 3d-4s band; thus the hole distribution is proportional to the electron density distribution. This fairly bold assumption is equivalent to assuming the cross section for exciting the electron to be independent of its position in the metal conduction band. In the analogous situation of an atom being excited by a projectile we know this is not true[7] and the excitation cross section does depend significantly on which electron is being excited; nevertheless the assumption provides a good starting point. Other simplifications are made following conventional practice for transitions in metal band structures including the assumption that transitions are direct. Utilizing Burdick's[6] calculations of band structure we have predicted the two theoretical bands shown in Fig. 1. Some limitations of the presentation must be born in mind. Firstly we have not yet corrected the observed spectrum for instrumental sensitivity; that correction will cause no change to the important features. Secondly the theoretical predictions need to be corrected for the spectrometer bandwidth and moreover the predictions do not take into account the broadening due to thermal vibrations of the lattice; the effect of these two corrections will be to smear out and probably eliminate all the sharper structure on the theoretical curves. One of the theoretical curves assumes that recombination occur only with electrons from the uppermost component of the conduction band ("Band 6" of Burdick's work); the other calculation assumes that recombination can take place with any electron in any band higher than the hole. This latter (i.e. including all bands) should perhaps be regarded as potentially the most accurate.

There are a lot of similarities between experiment and the predictions; the emission acquires an appreciable intensity at 2400 Å for all curves and all agree on a sharp drop at 3700 A. The bulk of the emission is contained between these wavelengths. One must remember that the prediction involves the quite unsubstantiated (and probably incorrect) assumption that the cross section for electron excitation (i.e. hole formation) is independent of the electrons original position. The next stage is to break this back down into contributions from the separate bands and determine some weighting factor for each, that will bring theory and experiment into better agreement; this weighting factor will essentially be the excitation cross section for the band. In view of the assumptions within the predictions at present, we regard the agreement here as most encouraging.

6. G. A. Burdick, Phys. Rev., 129 138 (1963).

7. E. W. Thomas "Excitation in Heavy Particle Collisions" (Wiley-Interscience 1972).

As yet we have not precited the recombination band shape for other metals but this is to be done soon. Aluminum will be the next case; the observed emission has quite a different form from copper (see Fig. 1) and there are extensive tabulations of theoretical band structure in the literature. We have already determined that the emission band for Al should have a weak onset at a photon energy of 5.44eV due to $\Sigma_3 \rightarrow \Sigma_1$ transitions; the onset will be weak, because the joint density of states is small along the $\Sigma_3 \rightarrow \Sigma_1$ line. The energy of 5.44eV corresponds exactly with the observed onset at around 2200 Å. Another similar weak onset should occur at a photon energy of 7.8eV ($\Lambda_1 \rightarrow \Lambda_1$ transition) but this is outside the spectral range we have used.

It is worth noting two related studies concerning broad band emission from solids, that have come to our attention. Mooradian[8] observed fluorescence of copper induced by an intense laser beam. Bonnot et al[9] record the "cathodluminescence" of copper; that is in fact the broad band emission induced by impact of 25 keV electrons on copper. In both these cases the emissions bear some resemblance to the ion-induced emission observed in our own work. Both of these publications invoke the mechanism of electron hole recombination to explain the observed emission and make some very vague references to the band structure of copper to justify this explanation. They do not however go as far as our own work and use the band structure to predict the form of the luminescence band.

In conclusion, we have excellent evidence that the broad band emission from the metal is due to the electron-hole recombination mechanism; detailed predictions of the spectrum expected from copper have been made.

What does this tell us about the solid state physics? In the first place we have identified the mechanism that causes emission and we have performed a prediction of the spectrum. Comparison between predicted and observed spectra will permit assessment of the accuracy with which band structures and transition matrix elements have been calculated. This will complement the results obtained by such methods as analysis of secondary electron spectra, X-ray appearence spectroscopy, and photo-electron spectroscopy. Furthermore, some of the transitions we expect, on theoretical grounds, should contribute to the spectrum are in fact absent or unexpectedly weak. This suggests that cross sections for excitation of the electrons (i.e. cross sections for hole formation) in certain bands, are very small. Thus we gain information on cross sections for electron excitation in the valence bands and therebye may better understand the mechanism wherebye ions deposit energy in a solid. This latter information has obvious technological implications for the understanding of the physical (and perhaps chemical) properties of ion-implanted materials and also for the predictions of the depth distributions of implanted ions.

8. A. Mooradian, Phys. Rev. Lets. 22, 185 (1969).

9. A. Bonnot, J. M. Deber, and J. Hanus, Solid State Communications, 10, 173 (1972).

(b) Alkali Halides

The alkali halides represent a group of materials with some well established regularities in the physics of their band structure. An added attraction was that there is quite a body of information on the luminescence of these materials when used as scintillators in nuclear physics. Samples of the spectra we observe under ion bombardment are shown in Fig. 2.

An important observation is that the emission from the alkali halides is as much as three orders of magnitude more intense than the emission observed when metals are bombarded. For ions on metals we have postulated above that the projectile collides with a "free" electron and excites it; because of the great difference between the ion and electron masses this is likely to be a very inefficient process and a weak recombination emission is to be expected. For the alkali halides it may be that the collisions of importance are those between projectile ions and lattice atoms; the similarity of masses ensures that momentum may be readily conserved and the excitation event involves an electron that is closely bound to the struck target atom. The cross section for such atom-atom collisions is expected to be high and the emission should be intense. The emission is expected to be related to the atomic structure of the individual lattice sites.

We have not yet had time to analyze these spectra in any sort of detail to confirm the above hypothesis. A brief examination of the data does reveal one feature that supports this picture and at the same time introduces a complicating feature. The NaCℓ spectrum shown on Fig. 2 has a number of regularly spaced bands around 5000 Å. These are identical to bands found by Rolfe et al.[9] in the u-v induced fluorescence spectrum of NaCℓ crystals grown in Oxygen. Rolfe et al.[10], seem to have shown quite conclusively that these bands are vibrational transitions of O_2^- ions located substitutionally at the $Cℓ^-$ sites of NaCℓ. Our crystals are supposed to be free of impurities so the O_2^- concentration must be very small. We also observe a group of lines around 3000 Å that have a very regular energy spacing (0.25eV) and which might also be due to a molecular structure; this spacing is in fact consistent with the emissions being from OH^- molecules.

Clearly the presence of impurities, even in very small quantities, may seriously confuse the analysis of the alkali halide spectra; this is not unexpected because the high efficiency of alkali halides as scintillators is directly related to low concentrations of impurities.

Our analysis of the alkali halide spectra is not yet very well developed and we expect to devote a substantial fraction of the remaining part of this grant period to that problem.

10. J. Rolfe, F. R. Lipsett, and W. J. King, Phys. Rev., 123, 447 (1961).

A Departure from the Original Program

In general we have followed closely the program contained in our original proposal. There is however one minor additional effort that we have performed as a service to another research group. Dr. Ben de Mayo, a faculty member of West Georgia College, is interested in the Mossbauer spectrum of iron and alloys. There is considerable interest in how the properties of iron are influenced by the introduction of hydrogen into the metal. It is hoped to understand how hydrogen leads to the embrittlement of steels. This is of obvious long term importance if hydrogen gas is to be used as an energy source when a "hydrogen energy-economy" becomes necessary.

The conventional technique for introducing hydrogen into metals is to simply heat the metal in hydrogen gas to promote the diffusion of gas into the sample. This is, however, not very effective as much of the hydrogen diffuses back out again as the metal is cooled. In the case of iron there is no net effect on the Mossbauer spectrum. I suggested to Dr. de Mayo that an alternative method for loading hydrogen into iron would be simply fire it in as a beam of ions from an accelerator. We have bombarded a number of iron samples with proton beams and delivered them to Dr. de Mayo for conventional Mossbauer analysis. It is observed that there is a substantial change in the Mossbauer spectrum of the implanted specimens; for example the hyperfine field increases by 3% over that for an untreated sample. Dr. de Mayo is working on an explanation of this effect which is based on the subtraction of electrons from the 4s band by the protons.

Our involvement in this side project is restricted to performing the actual bombardment of samples; all analysis is performed by Dr. de Mayo. The time involved represents only a few days of work and has not significantly detracted from the work we were committed to perform under this grant.

Program for the Remainder of the Grant Period

We shall complete our predictions of the copper luminescence band and perform the same analysis for aluminum. These two cases will then be published. Some attempt will be made to analyze the spectra we have recorded for other metals, but we expect only limited success in this since their band structures are not well understood. We shall also perform a detailed analysis of the spectra recorded for alkali halides.

Some additional recordings of spectra and measurements of intensities are planned for higher projectile energies (up to 1000keV). We anticipate that the spectra will change form under higher energy bombardment because electrons will be ejected from lower conduction band states and possibly also from inner shells of the lattice atoms.

If any further time remains available we shall commence the work contained in our renewal proposal.

Publications

The work is not yet at a stage that a detailed publication has seemed appropriate. We have, however, prepared two papers for presentation at conferences, the abstracts of which are published; copies of these are attached. Two detailed reports are presently being prepared and will be submitted to "The Physical Review" before expiring of the present grant.

(a) Conference paper; abstract published

"A Mossbauer Study of Hydrogen in Iron", (in collaboration with Dr. Ben de Mayo, West Georgia College). Contributed Paper, June meeting of the APS, Salt Lake City, Utah June 14, 1974. Abstract published in Bull. Am. Phys. Soc. 19, 675 (1974).

(b) Conference paper; abstract accepted for publication.

"Luminescence of Alkali Halides due to Ion Impact" Contributed Paper, Atlanta Meeting of the APS, Atlanta, Georgia, Dec. 5 1974. (Abstract to be published in Bull. Am. Phys. Soc.).

(c) Paper in preparation.

"Ion Induced Luminescence Spectrum of Copper", by M. Zivitz and E. W. Thomas (to be submitted to The Physical Review).

(d) Paper in preparation.

"Ion Induced Luminescence Spectra of Alkali Halides", by M. Zivitz and E. W. Thomas (to be submitted to The Physical Review).

Of the above reports the abstracts for (a), (b) and (c) are attached to this letter.

Theses None.

Inventions or discoveries None

Scientific Collaborators

Dr. Maury Zivitz - Post Doctoral Research Associate

Mr. Lynn Leatherwood - Graduate Student

Mr. Allan Carr - Graduate Student

Comments

The original proposal for this grant envisaged a two year effort; only the first year of this was funded initially. A proposal for renewal is being prepared along the general lines envisaged in our original proposal and with essentially the same budgetary provision that were contained therein.

Signature

E. W. Thomas

E. W. Thomas
Professor of Physics
Principal Investigator

29 Oct 1974
Date

xc. J. R. Stevenson, Director, School of Physics
J. Barbour, School of Physics (For file of G-41-630)
J. A. McPherson, ORA (For file of G-41-630)
H. S. Valk, Dean, General College

Attachments (i) Abstract for Salt Lake City Meeting of APS

(ii) Abstract for Atlanta Meeting of APS

(iii) Abstract of paper in preparation for publication.

EWT/jia

Abstract Submitted

for the Salt Lake City Meeting of the

American Physical Society

12-14 June 1974

Physical Review Analytical Subject Index Number 46.3

Bulletin Subject Heading in which Paper should be placed: Metals or Mössbauer Effect

A Mössbauer Study of Hydrogen in Iron.*
B. DE MAYO, West Georgia Coll., and E. W. THOMAS, Georgia Tech--Room temperature (RT) Mössbauer measurements have been made on a 0.001 inch thick iron foil bombarded with 20 keV protons. Assuming that all of the protons entered the foil, there were 4×10^{-3} protons per iron atom in the foil after bombardment. The effect of the protons was long range and increased the hyperfine field (H) from 329.1±0.5 kOe for the untreated foil to 340±0.5 kOe. After 47 days at RT, H decreased to 333.1±0.5 kOe, indicating that the hydrogen was diffusing out of the foil. The isomer shift decreased slightly (0.028±0.010 mm/sec) with bombardment and then increased with RT aging. The quadrupole splitting was negligible and the line widths were unaffected. All of the spectra showed only six lines. An explanation of the results which is based on subtraction of electrons from the 4s band by the protons will be discussed.

* Work supported in part by the Faculty Res. Comm. of W.G.C. and by NSF.

Submitted by

Benjamin de Mayo

Benjamin deMayo
Physics Department
West Georgia College
Carrollton, GA 30117

Abstract Submitted

for the Atlanta Meeting of the

American Physical Society

5-7 December 1974

Date

Physical Review
Analytic Subject Index
Number 13.2

Bulletin Subject Heading
in which Paper should be placed
Atomic Physics

Luminescence of Alkali Halides Due to Ion Impact.*

M. ZIVITZ and E. W. THOMAS, Georgia Institute of Technology--H°, H^{+}, He^{+}, and Ar^{+} particles produced by an rf type ion source were accelerated (5 → 30 keV), focused, and directed onto targets of NaCl, NaBr, NaF, and KF. Near UV and visible optical emissions from these targets were spectrally analyzed. Characteristic broad-band emissions were present under bombardment with each of the projectiles. In addition, Ar^{+} impact gave rise to strong emissions from sputtered target atoms. A series of seven equally-spaced emissions were observed in the case of NaCl. This series began at 3.8 eV; the members were spaced at 0.25 eV intervals and had full widths at half maxima of 0.1 eV. A comparison will be made between these emissions and published X-ray induced fluorescence spectra.

*Work supported in part by NSF.

Submitted by

Signature of APS Member

E. W. Thomas
Same name Typewritten

Georgia Institute of Technology
Address

Atlanta, Georgia 30332

Ion Induced Luminescence of Copper*

M. Zivitz and E. W. Thomas
School of Physics, Georgia Institute of Technology
Atlanta, Ga. 30332

(Received 1974)

The impact of 5 to 30 keV H^+ and He^+ ions on a polycrystalline copper target gives rise to emission of a broad spectral band extending from 3,000 to 5,000 Å with a definite peak at around 3,300 Å. It is shown that the emission is characteristic of the solid target and is not related to surface contamination. We postulate that the projectile ions excite electrons from the conduction band and that the resulting hole undergoes radiative recombination with an electron close to the Fermi level. Utilizing the detailed band structure calculations of Burdick it is possible to predict the general spectral distribution expected from such electron-hole recombination; the predictions are in good qualitative agreement with the observed light emission. Measurements of the emission intensity as a function of projectile energy are related to the cross section for excitation of the conduction band electrons.

*Supported by the National Science Foundation.

G-41-630

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332
November 1, 1974

SCHOOL OF PHYSICS

Dr. Richard Silberglitt
Solid State Physics Program
Division of Materials Research
National Science Foundation
Washington, D.C. 20550

Dear Dr. Silberglitt:

About one week ago I received from NSF an undated flyer headed "Organizational Changes" that indicates the timing for submission of such things as reports and renewal proposals. It seems that all the suggested deadlines were in fact passed before I received the reminder. I am sorry to be late but this is the first year I have held an NSF grant and I have had no prior experience of your schedules for such matters. I hope this late submission of material will not adversely effect my chances to get a renewal of this grant.

I am sending, under separate cover, a second letter to you that will serve as the "annual letter technical report" as stipulated in NSF publication NSF-73-12.

You also seem to need a "general interest" report suitable for documents prepared for Congress and the general public. A separate short report of this type is also included here; I hope it is not too "unscientific".

The reports include no information on employment of graduating Ph.D or Postdoctoral Fellows because none of the personnel that worked on this project in its first year have in fact left yet.

You will recall that my original proposal envisaged a two year effort and that you committed NSF funding for only one year. I assume that I must therefore submit another proposal to cover renewal for the second year. Such a proposal is now complete and requires only typing and administrative approval before sending to NSF; I anticipate you will receive it within two weeks. The scope of the proposed work and the budgetary provisions are essentially the same as were envisaged for the second year of our original proposal. I do hope that you can fund it so that the whole project may be completed as we originally intended.

Again my apology for being late with some of these items.

Yours sincerely,

E. W. Thomas.

E. W. Thomas
Professor

xc. J. R. Stevenson - Physics (For file of G-41-630)
J. A. McPherson - ORA (For file of G-41-630)

Research Highlights

Grant GK-40217

Georgia Institute of Technology

by

E. W. Thomas

Professor of Physics

24 October 1974

Collision Induced Optical Spectra of Solids

It has long been known that when an accelerated beam of ions strikes a metal, or other solids, there is an emission of light. In the case of metals, at least, there has been no serious investigation of the origin of such light emission. This research program is designed to investigate this phenomenon for both metals and insulators.

We take an ion beam from a small accelerator (5 to 30 thousand volts acceleration potential) and fire it at the target of interest. The emission is then analyzed by a conventional spectrometer to determine the wavelengths of the emission. An important experimental precaution is that the target material should be very clean and quite free of contaminants such as water, oil etc.. To ensure this, the samples are obtained highly pure (impurites less than a few parts per million) and then further cleaned. Finally the bombardment of the target takes place in a vacuum chamber at a pressure of less than 10^{-9} Torr or some twelve orders of magnitude less than normal air pressure. Specifically, we have used bombarding beams of hydrogen, helium and argon ions; five metal target have been used including copper and aluminum as well as four alkali halides including sodium chloride (common salt).

In the case of the metals the emission is very weak and to the eye appears to be of a blue color. Emission from the alkali halides is much more intense than that for the metals and is also frequently blue-green in appearance; an exception here is Sodium Fluoride that exhibits a bright red color. Detailed analysis of the spectra show three distinct features

(i) Spectral lines from projectiles that are reflected in an excited state.

(ii) Spectral lines from target atoms that knocked off (sputtered) by the incoming projectiles.

(iii) Broad spectral bands, extending over many thousands of Angstroms including visible and near ultraviolet regions.

This project is not concerned with the spectral lines from scattered projectiles or sputtered target atoms; the interest is in the broad band emisssions whose origin is unknown.

Much of our effort to date has been concerned with understanding the emission observed when copper is bombarded; copper is a metal for which there has been much previous work on solid state properties. When an assembly of copper atoms is coalesced to make a solid the seven outer electrons of each atom form a band of possible energy states. These electrons are essentially free to move around the metal and of course give rise to the excellent electrical conductivity properties of copper. We believe that the mechanism for light emission is as follows. An incoming projectile collides with one of the conduction band electrons and transfers some energy to it, removing it from its original position in the energy distribution and creating a hole (or "absence" of an electron). Subsequently a second electron falls into this "hole" and the energy it loses is emitted as radiation; such a process may be termed electron-hole recombination. On this basis one may calculate the shape of the spectrum emitted using other predictions of the conduction band structure; our calculation agrees very well with the spectrum that is observed. We are also busy attempting to calculate the recombination spectrum for aluminum and other metals.

In the case of the alkali halides (such as NaCℓ) we expect a similar process leading to emission. Here however, the electron that gets excited (and therefore the "hole" that gets created) may not free but rather are probably bound to a particular atom in the crystal. Again a higher lying electron can fall into the "hole" and give emission. Here the emission should bear some resemblance to the emission found when a single isolated atom is excited. We have shown that some of the emission from NaCℓ is in fact due to a small impurity concentration of Oxygen (in the form of O_2^-) located substitutionally at positions in the lattice normally occupied by Chlorine. The important thing is that the Oxygen emission is about the same as one would observe if the Oxygen were in fact free and not in the crystal. Our analysis of the alkali halides is continuing and by no means complete at the present time.

What are the implication of this? Firstly, of course, we have tentatively explained the phenomenon we set out to investigate. Secondly, we now know how the emission is related to established theory of the solid state and we can use the analysis of the emissions to assist with the further development of such theory. Finally, we are developing a detailed understanding of how accelerated ions deposit their energy in a target.

As with any "pure research" project it is difficult to document any immediate practical importance of the conclusions. We would however note that injection of ions into materials (ion implantation) is a new and novel technique for producing materials that cannot be created by conventional chemical methods. Such materials have very interesting electrical, mechanical and chemical properties; they are already used for semi-conductor device (e.g. transistors) fabrication, as cutting blades (to improve life of the

cutting edge) and as prosthetic devices (pins to join broken bones). Our work provides insight as to how the injected ion interacts with a target material and should assist with understanding of the novel properties exhibited by ion-implanted materials.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

April 14, 1976

SCHOOL OF PHYSICS

Dr. Dean Mitchell
Program Director
Solid State Physics Program
Condensed Matter Sciences Section
National Science Foundation
Washington, D.C. 20550

Dear Dr. Mitchell

This letter is to serve as the "annual letter technical report" as stipulated in NSF publication NSF 73-12. I do apologize for the fact that this report is late.

The highlights of this report are briefly as follows. We have shown that light ion (H^+ and He^+) impact on a clean aluminum surface gives rise to a broad band of luminescence which represents radiative electron-hole recombination; such mechanisms are of course well known in insulators and semi-conductors but rather unexpected in a metal. In studying ion-induced luminescence of alkali halides at temperatures from -100 to 200°C we find the principal mechanism is recombination of electrons with V_3 and V_4 centers; in fact the luminescence seems to closely follow the V_3 and V_4 center concentration as a function of such parameters as ion dose and temperature. We have identified a molecular spectrum peculiar to chemisorption of H_2O on NaCℓ and KCℓ; we tentatively ascribe this to H_2O molecules in a state which is perturbed by the surface. I would mention that this spectrum has also been seen in X-ray induced luminescence and has been ascribed to CN^- radical impurities; we have shown that the CN^- identification is incorrect. Finally we are continuing the study of broad bands induced by heavy ion (e.g. Ne^+, Ar^+, Kr^+, Xe^+) impact on transition metals; we have shown quite conclusively that this is observed only when oxygen is chemisorbed on the surface. These emissions are actually from sputtered metal oxides which are unstable in the ground state and never heretofore observed in conventional spectroscopic sources. We expect that these emissions will allow us to monitor the state of surface oxidation and perhaps provide information on the well known phenomenon of ion-beam-induced reduction of certain oxides.

In the preceding 12 months we have published one paper, had a second accepted and submitted a third. Two papers have been presented at conferences. Two Ph.D. students have been partially supported by this grant. Moreover, we have had the pleasure of being hosts to Dr. A. I.

Bazhin of Donetsk University USSR who is here under a USA/USSR government sponsored interchange; Dr. Bazhin has been entirely engaged in contributing to this NSF sponsored project.

The report on these activities is more fully contained in the following attachment, and some publications which are attached as appendixes.

I appreciate the opportunity to perform this research under NSF sponsorship and I trust that the continuation of this project will be scientifically fruitful.

Yours sincerely,

E. W. Thomas

E. W. Thomas
Professor

EWT:rh

Attachment (1) Detailed statement of activities.
(2) Three Appendixes in the form of publications or pre-prints.

xc: J. R. Stevenson
H. Valk (For file of G-41-630)
J. McPherson ORA (For file of G-41-630) 7 copies

Attachment to Letter of 14 April 1976

Progress Report

Name of Institution: Georgia Institute of Technology

Name of Principal Investigator: Professor Edward W. Thomas

Grant No.: DMR73-02317 A01

Starting Date: 1 April 1975

Completion Date: 31 March 1976

Grant Title: "Collision Induced Optical Spectra of Solids"

Description of the Research

The program is designed to study excitation effects in solids, or on solid surfaces, which occur under bombardment with 10-30 KeV ion beams. The experimental technique is to record and measure the optical emissions at the point where an ion beam strikes a surface. The spectra of interest are broad continua having little identifiable structure; we are not concerned with atomic line emissions from reflected projectiles or sputtered atoms.

Our studies have shown that there are two classes of phenomena. One class involves excitation mechanisms associated with the chemical structure of the surface and materials deliberately absorbed thereon; the second class are emissions from the bulk of the material and are in a sense intrinsic phenomena related to the band structure of the solid. Emissions from surface structure and absorbates shows some potential for studying chemical reactions at surfaces; such emissions are proving difficult to interpret since the

molecular species are apparently quite different from compounds studied by conventional spectroscopy in the gas phase. However, our studies of emission from the bulk have been quite readily, and successfully, interpreted by reference to other published work on electronic band structures and radiation induced defect centers.

Our program has evolved into a study of various distinct phenomena and further discussion will be subdivided to represent the separate mechanisms of the various emission phenomena. We shall commence with a discussion of the surface and chemical effects which represent the present focus of our work and are not yet published. Later we shall deal with the bulk phenomena and rely primarily on re-prints and pre-prints of our published work. We shall not describe the apparatus and procedures since these are adequately covered by the appendixes and references cited therein.

A. Surface Related Excitations

(a). Transition Metals.

One of the strangest phenomena observed in ion-induced luminescence is a broad spectra band induced by heavy ion (Ne^+, Ar^+, Kr^+) impact on certain metals, notably Mo, W, Ti, Cr, Ta and Zr. The most surprising feature is that the source of emission extends a centimeter or so in front of the target. As yet there are no published discussions of this phenomenon but three papers are due shortly[1] by groups at Bell Laboratories, FOM Amsterdam, and Gorki University (USSR). In our own recent work we have shown conclusively that the phenomenon occurs only when oxygen is absorbed on the surface. We can deliberately introduce oxygen into the vacuum system and study the emission

1) To be published in Nucl. Instr. and Meth. 132. By White et al., Kerkdijk et al., and Kijan et al.

intensity as a function of that pressure; the surface coverage of oxygen will be governed by the rate of oxygen arrival from the gas phase and the rate of removal of oxygen by sputtering. Thus by altering ambient gas pressure, or incoming beam current, one can change the equilibrium surface coverage. We find that no emission of these bands occurs at ambient pressures below 3×10^{-9} torr but above this the intensity rises rapidly; above about 10^{-7} torr certain spectral features reach a constant intensity and other features begin a rapid decline with further pressure rise. The behavior is a function of ion beam current density as one might expect; the ambient pressure of 10^{-7} torr corresponds to a surface coverage of about one monolayer for the beam currents we employ. If the oxygen is removed, then the emission persists for many seconds having a decay time appropriate to the sputtering away of the oxygen surface coverage. This latter observatory shows that the emission is due directly to sputtered particles and is not from the interaction of sputtered particles with the ambient gas atmosphere. If a cleaned surface is exposed to oxygen without the presence of the ion beam, then no emission is observed; this rules out chemisorptive luminescence recently found[2] with Aℓ and Mg exposed to O_2. The phenomenon is only found with O_2 gas exposure; with H_2, Ar, N_2, CO no emission of bands is seen.

In the attached Figure is the spectrum we observe with an Mo target; there are various sharp features on an underlying continuum. The sharp peaks around 380-390 nm are from sputtered Mo atoms and are also observed with no oxygen present; the remainder of the spectrum is broad bands which show no structure with resolutions as high as 0.1 nm. We also have spectra for W and Nb with similar general characteristics. The spectral form of these bands

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2) B. Kasemo, Phys. Rev. Letts. 32, 1114 (1974).

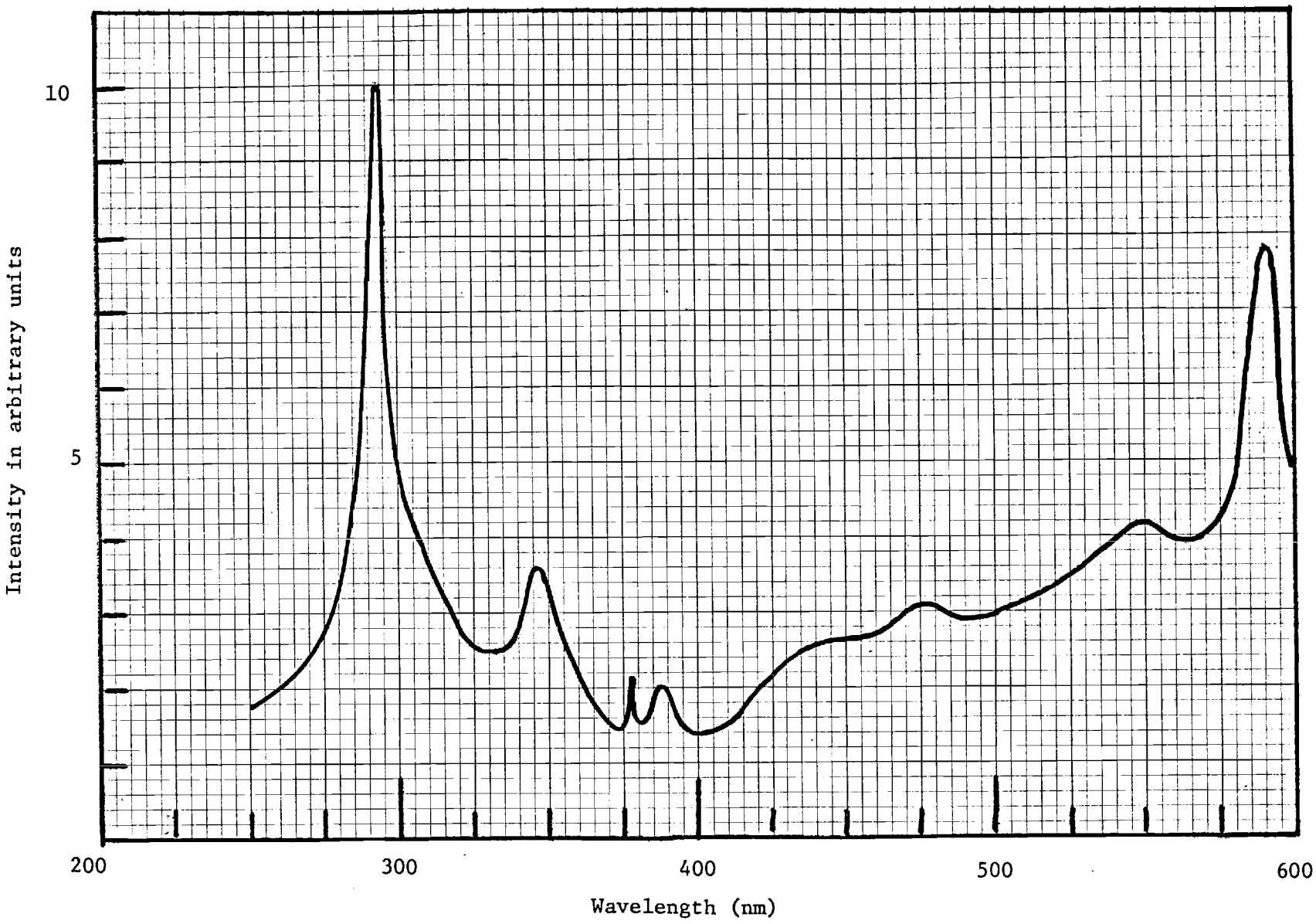

Figure. Typical spectrum observed when molybdenum is bombarded by Ar^+ in the presence of ambient oxygen. The small peaks at around 380 - 390 nm are from sputtered Mo atoms. The major peak at 295 nm remains unresolved at resolutions to 0.1 nm.

is completely consistent with the decay of a molecule to a shallow repulsive state[3] and is similar to that found for rare gas-alkali metal dimers[3] which are currently exciting interest for use in lasers. Since the emission is seen outside the surface, the molecule must have been ejected by the projectile impact. Tests have shown that the emission sources are not charged. All evidence is quantitatively consistent with the source of emission being an unstable neutral oxide molecule ejected from the surface.

Unfortunately there is little or no published information on the emission spectra of molybdenum oxides, and we have not definitely identified the species involved. A significant test that we have recently performed is to bombard Mo O_3 with Ar^+. We observe an emission spectrum that is identical in all respects with that observed for Ar^+ on Mo in the presence of O_2. Thus it seems clear that the observed emission is due to a sputtered oxide of molybdenum; from the spectroscopic characteristics we believe that the sharp peaks shown on the figure are Mo O^*. The underlying continuum, extending over the whole spectrum, shows some different characteristics with pressure compared to the sharp peaks. It is possible that this represents a second oxide species.

The impact of heavy ions on molybdenum oxide is known to produce a reduction of the insulating Mo O_3 to the metallic Mo O_2 form[4]; this has some possible applications to integrated circuit fabrication[4]. If indeed the observed spectral features are associated with different oxide states then this optical emission provides a method for monitoring the chemical changes while the ion beam is causing the reaction.

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3) M. F. Golde, J. Mol. Specy. 58, 261 (1975).

4) H. M. Naguib and R. Kelley, J. Phys. Chem. Solids 33, 1751 (1972).

Certainly the origin of this emission is not yet properly defined. We are attempting first to identify the emitting species and then we shall relate their intensity to oxygen surface coverage determined by some separate technique (such as ellipsometry). We shall perhaps then be able to use this understanding for a study of how oxygen interacts with Mo in the presence of an ion beam. Apart from the possible implications for study of surfaces, we can quite definitely state that this phenomenon provides a new type of light source with which the spectroscopist can study exotic molecules that are not accessible in more conventional spectroscopic sources.

(b). Contaminants on Alkali Halide Surfaces.

We have frequently observed a distinct band structure at around 270 nm when NaCℓ is bombarded by light ions (H^+, He^+); there are some seven peaks, regularly separated in photon energy by 0.25 eV and having a width of about 3 nm. Such regularity is expected only for a simple molecular structure. The emission is undoubtedly due to a surface contaminant since it is removed by conventional cleaning procedures such as heating and sputtering.

Recently an identical spectrum has been observed[5] in the X-ray induced fluorescence of certain alkali halides deliberately doped with CN^- radicals; the spectra was ascribed[5] to substitutional CN^- radicals at halide sites. There is no doubt that our ion-induced band spectrum and the published X-ray induced band spectrum are spectroscopically identical. We find, however, that the spectrum observed in ion-induced luminescence is directly associated with adsorption of H_2O onto the crystal surface. We are unable to generate this spectrum by adsorption of gases containing C, N or combinations of these elements.

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5) E. Von Heyden and F. Fischer, Phys. Stat. Sol. (b) 69, 63 (1973).

This forces us to conclude that the fluorescence ascribed by Von Heyden to CN^- is incorrectly assigned and rather is related to H_2O, or OH. We note that the crystals used by Von Heyden were not maintained in a vacuum environment and that the absorption spectra of these crystals differ from all other published work with CN^- doped alkali halides.

The observed bands do not correspond to the well known fluorescence spectra of OH^-[6] nor do they show any obvious similarity to gas phase spectra of OH or H_2O molecules. However, the line spacing of 0.25 eV is identical to the vibrational spacing of H_2O absorption bands in the infra red; peak widths are also similar to those found in i-r absorption. This would seem to be strong evidence (though not conclusive evidence) that our bands are due to adsorbed H_2O. Since the bands do not closely correlate with gas phase emission spectra we must conclude that the H_2O is perturbed by the surface.

Behavior of the band intensity with ion dose and target temperature is consistent with excitation of the molecular state by migration of F-centers to the crystal surface. We are about to test this by the simple technique of F-center optical bleaching; we anticipate that the band intensity will be reduced by such quenching.

B. Excitation in the Bulk

(a). Metals.

In our studies of luminescence induced by light ions (H^+ and He^+) on clean metal surfaces we have discovered a very strong intrinsic luminescence in aluminum and very weak luminescence of metals such as Cu and Mo. These observations have been briefly reported and a full report is to be published

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6) H. J. Maria and S. P. McGlynn, J. Chem. Phys. 52, 3402 (1970).

7) J. G. Bayly et al., Infra Red Physics, 3, 211 (1963).

within weeks[8,9]; we attach copies of both papers and content ourselves here with reproducing the abstract of our second publication[9].

"Impact of 10- to 30-keV H^+ ions on polycrystalline Al, Cu, and Mo targets induces broad-band light emissions in the photon energy range of 2-6 eV; these emissions emanate from the target. For aluminum the emission is particularly intense, increases linearly with incident beam current, and is invariant in relative shape with projectile energy and angle of incidence. The dominant peak is at a photon energy of 2.4 eV; and a weak shoulder is observed at 3.3 eV. An electron-hole recombination model is shown to account for the general form of the emission band. We also calculate the electron density of states and the complex part of the dielectric constant ε_2; the energy-band structure based on Ashcroft's Al pseudopotential is presented in tabular form."

It should be noted that emission from Mo described herein, under H^+ and He^+ bombardment, is for an atomically clean surface. It is both spectroscopically different and weaker (by three order of magnitude) than the emission observed when Mo is bombarded with heavy ions in the presence of O_2; thus it is a different emission than that described under A(a) of this report.

(b). Alkali Halides.

We have studied the luminescence induced by 10-30 KeV H^+ and He^+ ions on various pure alkali halides (NaCℓ, NaF, KCℓ, KBr) at "high" temperatures

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8) M. Zivitz and E. W. Thomas, Nucl. Instr. and Meth. 132, 411 (1976). (Attached as Appendix I).

9) M. Zivitz and E. W. Thomas, Phys. Rev. B, (To be published) April 1976. (Attached as Appendix II).

(-160°C to 200°C). The work has been submitted for publication[10] and we shall content ourselves here with reproducing the abstract:

"A study has been made of luminescence induced by 25 keV H^+ and He^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependence of luminescence, and the effect of bleaching, in KCl and KBr. The peak intensity in the luminescent spectrum is independent of temperature from -160°C to -70°C, rises to a maximum at about -10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole-centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to O_2 we also observe an additional band characteristics of O^-_2".

Conclusion

The work on ion-induced luminescence of pure alkali halides and of clean metal targets has been brought to a successful conclusion. Our efforts are currently devoted to spectra observed when surfaces are deliberately covered with a known absorbate. The understanding of spectra induced by bombardment of adsorbed layers is by no means complete, but we have ample evidence that it is closely related to the chemical situation of the adsorbate.

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10) A. I. Bazhin, E. O. Rausch, E. W. Thomas, Phys. Rev. B (Submitted for publication and attached as Appendix III).

It would obviously be desireable to combine our optical studies with a parallel direct study of surface chemistry by such conventional techniques as LEED or Auger spectroscopy. While the required equipment for is not available in the writer's laboratory, we do hope to perform some studies along these lines by co-operation with other groups.

Publications, Papers and Seminars

Publications

(1) "Ionoluminescence of Aluminum". M. Zivitz and E. W. Thomas, J. Nucl. Mat. 132, 411 (1976).

(2) "Ionoluminescence of Aℓ, Cu, and Mo; Optical Properties of Aluminum". M. Zivitz and E. W. Thomas. Phys. Rev. B (to be published April, 1976).

(3) "Luminescence Induced by Ion Impact on Alkali Halide Crystals at High Temperatures (-160°C to 200°C). A. I. Bazhin, E. O. Rausch and E. W. Thomas. Phys. Rev. B (Submitted for publication).

Papers Presented at Conferences

(4) "Luminescence of Alkali Halide Monocrystals Induced by Ion Beam Excitation", March Meeting of the APS, Atlanta, Georgia April 1, 1976. Published in Bull. Am. Phys. Soc. 21, 438 (1976).

(5) "Ionoluminescence of Aluminum". Contributed Paper; VIth International Conference on Atomic Collisions in Solids, Amsterdam, September 1975.

Seminars Related to this Work

(6) "Scattering of Atoms in Gases and at Surfaces". Seminar, University of Oklahoma, 1 April 1975.

(7) "Scattering of Atoms in Gases and at Surfaces". Seminar, University of Missouri, Rolla, Mo., 2 April 1975.

(8) "Light Emission Induced by Ion Impact on Surfaces". Seminar, Sandia Laboratories, 2 Dec. 1975.

Theses

"Optical Investigations of Ion-Metal Collisions" by W. E. Baird (Nov. 1975).

Scientific Collaborators

Dr. W. E. Baird - Graduate Student

Mr. J. E. Harriss - Graduate Student

Dr. A. I. Bazhin - Soviet Exchange Scholar

Dr. O. Rausch - Postdoctoral Research Associate

Dr. M. Zivitz - Postdoctoral Research Associate

(Note: Bazhin, Rausch and Zivitz receive no financial support from this grant).

Inventions or Discoveries None.

Signature

E. W. Thomas

E. W. Thomas
Professor of Physics
Principal Investigator

April 16, 1976
Date

xc: J. R. Stevenson, Director, School of Physics
J. Barbour, School of Physics (For file of G-41-630)
J. A. McPherson, ORA (For file of G-41-630)
H. S. Valk, Dean, General College

Appendix I

NUCLEAR INSTRUMENTS AND METHODS 132 (1976) 411–414; © NORTH-HOLLAND PUBLISHING CO.

IONOLUMINESCENCE OF ALUMINUM*

M. ZIVITZ and E. W. THOMAS

School of Physics, Georgia Institute of Technology, Atlanta, Ga. 39332, U.S.A.

The impact of low energy (10–30 keV) H^+ and He^+ ions on polycrystalline aluminum gives rise to broad band optical emission; this extends from 3000 to 6500 Å and peaks in intensity near 5100 Å. The integrated intensity in this band represents approximately 0.02 photons emitted for each ion incident. All observations are consistent with the source of the emission being localized in the target surface. We suggest that this emission is due to a recombination mechanism involving electrons localized (in reciprocal space) at a minimum in an excited band at the critical point W. We calculate the spectral distribution expected from this direct-transition, electron–hole recombination model and show that the result is consistent with the observed spectrum.

1. Introduction

Fast ion impact on solid surfaces results in several types of emission in the near uv region of the electromagnetic spectrum. We are here concerned with a broad band of emission, extending over the visible and near uv regions, which is observed when H^+ and He^+ ions are incident on aluminum. Such bands can be readily distinguished from the characteristic line emissions emitted by sputtered target atoms and backscattered projectiles.

There are a number of earlier reports[1,2]) identifying broad band emission induced by ion impact on solids but as yet no explanation of the emission mechanism. In this paper we consider the specific case of aluminum and show that a direct interband recombination transition will give a spectrum similar to that which is observed. In many respects our model is similar to the established picture of luminescence in insulators and semiconductors.

2. Experimental details and results

The experimental arrangement is identical to that described in a previous publication[3]), and we refer the reader to that earlier work for complete details. Ions are produced by an rf source, accelerated, mass analyzed, and directed onto some target surface at an angle ϕ to the surface normal. A grating monochromator is placed perpendicular to the ion beam with its axis in the plane defined by the incoming beam and the target surface normal; the monochromator views the point of beam impact on the surface through a sapphire window. Detection efficiency of the optical system has been established by calibration against a standard lamp. The targets were polycrystalline aluminum of high purity. Before use they were mechanically polished. The target chamber was ion-pumped to a background pressure of 10^{-9} torr. It was possible to sputter-clean the target by using an Ar^+ beam from the accelerator.

In fig. 1 we show the broad band spectrum from aluminum corrected for variations in spectral detection sensitivity. For He^+ impact the spectrum is similar. In addition to the broad band, there are some emissions from backscattered projectile atoms and sputtered target atoms. These characteristic atomic line emissions will be discussed elsewhere[4]) and have been removed from the spectra of fig. 1 to prevent confusion. We would note that the spectra of fig. 1 were taken with 15 Å resolution; use of higher resolution reveals no structure on the curves. Although changes of incidence angle and incident projectile energy did cause alterations in intensity, they caused no discernible change to the relative shape of the spectral line. The integrated intensity under the curve between 3000 and 6500 Å represents 0.02 photons per ion incident.

Considerable precautions were taken to ensure that this emission did indeed arise at the point of beam

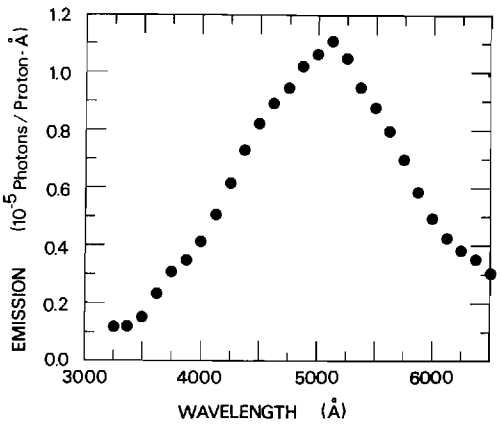

Fig. 1. Luminescence spectra of Al, induced by 25 keV H^+ impact at an incidence angle of 45°.

* Supported in part by the National Science Foundation.

impact on the surface. We made tests to confirm that the sapphire window on the target chamber was not fluorescing. We attempted to monitor the spatial distribution of the emitters and concluded that they were located at the surface. It was shown that band intensity increased linearly with beam current up to our maximum densities of 30 μA/cm^2. We did observe the emissive intensity to vary with time when the projectile beam was first directed onto the target. The intensity decreased for some minutes and then stabilized. We concluded that this represented the effect of surface contamination and that after the surface was properly cleaned by sputtering the intensities reached their equilibrium value. During these initial unstable conditions the shape of the band spectrum did not change, only its intensity decreased. With these various precautions we conclude that the emission is not due to any artifact of the experimental system and does truly represent the effect of ion impact on the surface.

3. Possible emission mechanisms

The range of a 25 keV proton in aluminum is some 2000 Å. The absorption coefficient for visible light in aluminum is of the order 10^6 cm^{-1}; it follows that emission can only escape from a depth of about 100 Å below the surface. Therefore the emitting sites must be located either at the surface itself or within a section of the material which is only about 100 Å deep and consequently very much less than the projectile range. It is quite easy to show that for emission sites located at, or close to, the surface, the intensity should vary as the tangent of the incidence angle ϕ. Experimental tests show that this is approximately true.

It is also worth bearing in mind that the emission of light represents only a very small faction of the energy lost by the projectile. For 25 keV H^+ impact the projectile loses many kilovolts of energy to the solid within the optical skin depth; by contrast only about 0.02 photons are emitted for each ion incident on an aluminum target and such photons have an average energy of 2.5 eV. Clearly, photon emission into the broad band represents only a small fraction of the energy transferred to the solid.

We did consider the possibility that the emission could be either transition radiation or Bremsstrahlung. For both these mechanisms the emissions should be polarized; we observed no polarization. Moreover one may estimate reliably the intensities to be expected for both these mechanisms; the predicted intensities are seven order of magnitude lower than what we observe. Consequently we reject these two mechanisms.

We propose that the emission from aluminum is due to an electron hole recombination mechanism; the initial excitation being provided by the interaction of the projectile with valence electrons. Bonnot et al.[5]), have previously invoked a recombination mechanism to explain cathodoluminescence in copper, although they make no attempt to predict the spectrum in detail. To test the recombination mechanism one should be able to take the tractable, pseudopotential band structure of aluminum and predict the expected emission band. The objective is to show qualitative agreement between the location of the predicted and observed bands. Because of certain simplifications in our development of the calculation we do not anticipate a close quantitative agreement in spectral shape.

4. The recombination mechanism

Impact of projectiles on the target causes excitation of electrons and results in a continuous generation of holes in the valence band. It is presumed that electrons radiatively recombine with these holes. It is assumed that recombination occurs by direct (vertical) interband transitions involving initial and final states which lie at the same point (wavevector $\boldsymbol{k}$) in the first Brillouin zone (reduced zone scheme). We neglect thermalization (rising of holes and falling of electrons due to photon emission) of the excess carrier distribution generated by ion impact. We assume this to be a small frozen distribution in excess of the equilibrium distribution and that the Fermi level is unpertubed. We have by definition at wavevector $\boldsymbol{k}$

$$E_i(\boldsymbol{k}) - E_F(\boldsymbol{k}) = E, \tag{1}$$

where $E = \hbar\omega$ is the emission photon energy, $E_i(\boldsymbol{k})$ is the initial band energy and $E_f(\boldsymbol{k})$ is the final band energy. The joint density of states for emission can be written

$$J(E) = \frac{2}{(2\pi)^3} \sum_{i,f} \int_{\mathrm{BZ}} \mathrm{d}^3\boldsymbol{k}\, \delta[E_i(\boldsymbol{k}) - E_f(\boldsymbol{k}) - E]. \tag{2}$$

The integration is carried out over the whole Brillouin zone (BZ) for a given band pair, and the calculation is repeated for each pair of bands i, f.

To write an expression for recombination rate we must include the distribution of electrons and take into account the matrix element for the transition. Following Mooradian and Fan[6]) we write the recombination rate as follows:

$$r(E) \propto E \sum_{i,f} \int_{BZ} d^3k \, |M_{if}(\boldsymbol{k})|^2 \times$$
$$\times f_i[1 - f_f] \, \delta[E_i(\boldsymbol{k}) - E_f(\boldsymbol{k}) - E]. \quad (3)$$

This expression gives the rate at which photons of energy $E = \hbar\omega$ are emitted per unit energy interval $dE = \hbar d\omega$. The matrix element $|M_{if}(\boldsymbol{k})|$ is related to the pseudo wavefunctions for the initial and final states. f_i represents the distribution of final states or the distribution of holes with which the electron recombines. To proceed with a calculation of recombination rate one must calculate the matrix elements and decide on some values for the state distributions f_i and f_f.

The calculation of emission spectra is a tedious but straightforward procedure. We generated the energy band structure and wavefunctions using an empirical pseudopotential model with four orthogonalized plane waves. The energy bands, which we do not give here, were very similar to those of Ashcroft[7]). To test the matrix elements generated with our wavefunctions we calculated the complex part of the dielectric constant ε_2, and found it to be in good agreement with the calculations of Brust[8]).

Two different models were tried for the recombination process, involving two different state distributions. For the first model we supposed that the recombining electron comes from some point below the Fermi level. There are three bands below the Fermi level so our recombination mechanism involves a transition from band 2 to 1, or 3 to 1, or from 3 to band 2. We let the following describe the distribution functions:

$$f_i = 0, \qquad E_i > E_F, \quad (4a)$$

$$f_i = 1, \qquad E_i \leq E_F, \quad (4b)$$

$$f_f = \sigma, \qquad E_f < E_F. \quad (4c)$$

Eq. (4a) says that no recombining electrons lie above the Fermi level E_F. Eq. (4b) indicates that the Fermi distribution function holds below the Fermi level, $f_i = \{1 + \exp[(E_i - E)/kT]\}^{-1}$; for low temperatures we can approximate f_i by unity. Finally in eq. (4c) the holes or final states are represented by a small arbitrary constant. This set of conditions means that the electron distribution was essentially unchanged by the collision process and that hole formation is very small and uniformly distributed throughout the band structure. This latter assumption is equivalent to assuming that the cross section for electron excitation in the solid is independent of the electron's initial energy. The result of this model is included in fig. 2.

The second model considered is similar to the established picture[9]) for recombination in insulators and semiconductors. Inspection of the aluminum band structure[7]) shows that the first excited band (band 4, which lies above the Fermi level), has a minimum at the critical point W. Any electron excited from bands 1, 2 or 3 to band 4 may reach the W point by phonon emission. Further decay can only be radiative since the minimum at W is energetically isolated from the other bands. In the spirit of the calculation we arbitrarily let the 4th band be occupied up to 0.5 eV above the minimum at the W point. Again we assume the generated holes are isotropically distributed. The following distribution describes the perturbed metal:

$$f_i = 1, \qquad (E_{4,\min} + 0.5\ \text{eV}) \geq E_4 \geq E_{4,\min},$$

$$f_i = 0, \qquad E_4 > (E_{4,\min} + 0.5\ \text{eV}),$$

$$f_f = \sigma, \qquad E_f \leq E_F.$$

Only band 4 was used as a source of initial states; $E_{4,\min}$ denotes the band minimum.

The emission spectra calculated from these models are shown in fig. 2 along with the experimental emission. It should be noted that only the experimental data is absolute; both predicted curves have been fixed to facilitate comparison with experiment.

We regard the degree of correspondence between experiment and model two as encouraging; this is the model where recombination involves excited electrons and is similar to the process used to explain luminescence in insulators and semiconductors. Our objective

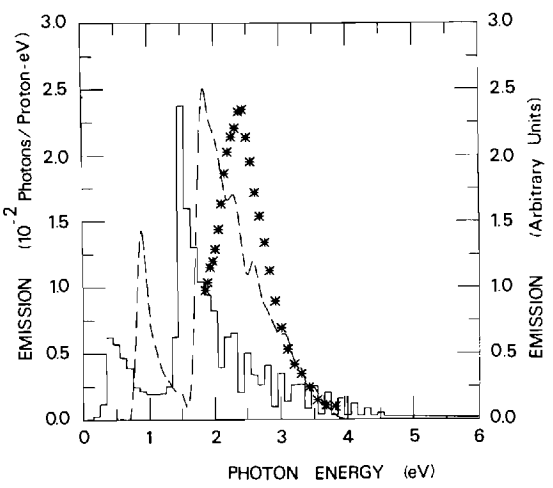

Fig. 2. Theoretical emission spectra according to models I and II (arb. units) compared with the absolute value of the experimental emission. Histogram, model I; dashed curve model II; stars experimental emission.

was to determine whether emission is predicted to occur at the wavelengths where it was observed; clearly the model does this. One of the major inadequacies in the theory is that we have assumed the electron hole pairs to be uniformly distributed throughout the available bands; this assumption also means that we essentially ignore all details of the collisional excitation process. We could force a better agreement between theory and experiment by adopting suitable excitation distribution functions so that the shape of the predicted intensity distribution agrees better with experiment.

There seems to be little correspondence between experiment and the calculations by the first model. The predicted peak is at 1.5 eV, quite significantly removed from the experimental peak at 2.3 eV. More important the observed intensities are most significant at photon energies where the predicted intensities are 5% or less of the maximum. Thus the first model does not clearly satisfy our basic criterion of predicting the range of photon energies where the greatest intensities are observed.

In conclusion, the second recombination model is consistent with observations. That model assumes recombination of excited electrons (in band 4) with holes generated in the conduction band. The agreement is qualitative only, and for further improvement one must take into account a variation of electron excitation cross section across the valence bands.

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Ionoluminescence of Al, Cu, and Mo: Optical properties of aluminum*

M. Zivitz and E. W. Thomas
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 21 July 1975)

Impact of 10- to 30-keV H^+ and He^+ ions on polycrystalline Al, Cu, and Mo targets induces broad-band light emissions in the photon energy range of 2–6 eV; these emissions emanate from the target. For aluminum the emission is particularly intense, increases linearly with incident beam current, and is invariant in relative shape with projectile energy and angle of incidence. The dominant peak is at a photon energy of 2.4 eV; and a weak shoulder is observed at 3.3 eV. An electron-hole recombination model is shown to account for the general form of the emission band. We also calculate the electron density of states and the complex part of the dielectric constant ϵ_2; the energy-band structure based on Ashcroft's Al pseudopotential is presented in tabular form.

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I. INTRODUCTION

Fast-ion impact on solid surfaces results in several types of radiant emission in the visible and near-uv region of the electromagnetic spectrum.[1,2] Doppler-shifted atomic line emissions emanate from backscattered excited projectile atoms or ejected target atoms.[3-5] Characteristic band emissions result from excited electrons within insulators and semiconductors; broad-band light emission has also been observed due to ion impact on metals.[3,6] Here we report quantitative measurements of luminescence induced by 10- to 30-keV H^+ and He^+ impact on a variety of metals. Spectra took the form of bans (~1000- to 2000-Å full widths) observed in the photon energy range 2–6 eV. These bands were readily distinguished from atomic line emissions. For Al we observed emissions characteristic of the electrons within the solid. Several mechanisms have been previously suggested as sources of this or similar emission.[3,7,8] In this paper, we consider several of these models further.

In Secs. II and III we present our experimental results and a discussion of these spectra. Section IV contains a few of the mechanisms we considered and the reasons for discarding them. These models were bremsstrahlung, transition radiation, and recombination radiation due to the decay of surface plasmons. This is followed in Sec. V by a theoretical treatment based on direct interband transitions for the emission in Al, which is shown to account for the observed spectrum.

Two calculations are made, to account for the source of the Al band. One prediction is based on a generalization of a model proposed by Mooradian in a study of photoluminescence of noble metals.[7] This model is essentially electron-hole recombination by means of direct interband transitions between an occupied state (below the Fermi level) and a vacancy (created below) by ion impact. We take the cavalier view of neglecting the thermalization of the carrier distribution which exists in excess of the equilibrium distribution. The second model is similar to the established picture of luminescence in insulators and semiconductors.[9] The calculations use Ashcroft's empirical pseudopotential.[10] We present analytic solutions for the roots of the four-band secular determinant at several symmetry points of the Brillouin zone. These solutions are of interest as they provide energy gaps which differ slightly from the commonly quoted two-band gap result $E_g = 2V_{\vec{G}}$.

As a check on our numerical procedures, we compute the electron density of states and compare the resultant Fermi level with Ashcroft's result (Ashcroft obtained his Fermi level in a quite different manner). We compute the complex part of the dielectric constant ϵ_2, as a check on our matrix elements. Fair agreement is obtained as 0.5 eV and excellent agreement is obtained at 1.5 eV with the nine-band model of Brust.[11]

Section V contains a brief comparison between experiment and theory. The Appendix contains the band structure of Al on a mesh convenient for tabulation.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The apparatus used in these luminescence experiments has been previously described.[5] Ions from an rf discharge source were momentum analyzed, collimated, and directed onto polycrystalline target surfaces at some angle ϕ with respect to the target-surface normal. Emissions from these targets were viewed at 90° to the incident beam by a grating monochromator, followed by a photomultiplier tube provided with photon-counting instrumentation. Projectiles of H^+, H^0, and He^+ at 5- to 30-keV impact energy provided ~1-μA

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THANK YOU.

iclusively that window fluorescence was not the gin of the emission. Other tests included bias- the target to suppress secondary ions and elec- ns; this causes no change to the observed spec- . To ensure that targets were free of contami- ion they were subject to bombardment by argon neon ion beams for extended time periods to rmit sputter cleaning. The form of the broad id emissions was unaffected by this treatment. n the case of aluminum and copper, targets we ide tests to ensure that the broad-band emissions anated from the target surface and not from me range in front of these surfaces. The optical stem (see Fig. 1) was provided with a series of ffles so that the field of view at the target was stricted to a width of 2 mm in the plane of the n beam. The target was set at an angle ϕ of 45° d irradiated with a beam collimated to 2-mm ameter. Then the target was translated along e beam path for a distance of 7 mm to either de of the intersection of the monochromator axis th the ion-beam axis; the spectrum was moni- red as a function of the target position. At a rget displacement of ±2 mm from the intersec- on of the ion beam and optical axis, the intensity all spectral components was negligible. This dicates that the source of emission occupied a egion of 2 mm extent in the plane containing the n-beam axis; this is exactly the region irradiated the ion beam. As a further test the angle of eam incidence ϕ was set at zero degrees and the ptical system, with the 2-mm field of view, was rranged to view a region centered at 1 mm in ront of the surface; no optical signals were ob- erved. Allowing for statistical variations in sig- als and mechanical errors in defining position, e consider the accuracy of the location of the source of emission to be about 0.5 mm. Thus, our observations show that the source of emission lies at the surface, or certainly no more than 0.5 mm in front of the surface. Because of the necessity of using mechanical systems for this test it is not feasible to appreciably improve the spatial resolution. We conclude that there is no evidence that the source of continuum emission does not lie in the surface.

From the above tests of spatial distributions one can also derive some information on the velocity distribution of sputtered atoms. With He^+ impact on Al we can also observe emission from sputtered aluminum atoms in the multiplets at 3089 and 3956 Å. These exhibit the same spatial distribution as the continuum emission. Utilizing the known lifetimes of these excited aluminum states[17] we estimate the average velocity of the sputtered aluminum atoms to be less than 5×10^5 cm sec^{-1}. There have been no measurements of sputtered aluminum velocity distributions. However, if one uses the simple theoretical estimate of average sputtered particle energy given by Dearnaley *et al.*,[18] and a cohesive energy for aluminum[19] of 3.34 eV/atom one gets an average velocity of 10^5 cm/sec; this is consistent with our observations.

There have been various previous studied of luminescence in metals where broad-band light emission has been observed. Van der Weg and Lugujjo[5] osberved emission induced by 40-keV Ar^+-ion impact on various metals; they found broad bands only when the *d* bands of the metals were half-filled (notable Mo). Mooradian[7] reported a photoluminescence in Cu with peak emission at 2 eV. Our spectra do not correlate with any of these previous observations. Bonnot *et al.*[8] report spectra induced by 25-keV electron impact on cop-

TABLE I. Observed emissions and relative transition rates at band maxima, for 25-keV H^+ and He^+ impact on various metals at 60° angle of incidence. For each projectile the rates are normalized to 100 arbitrary units; a blank denotes negligible emission. No correction for spectral transmission function of system has been used here.

		Band I		Band II	
Projectile	Target	location (Å)	strength (relative)	location (Å)	strength (relative)
H^+	Al			5200	100
	Cu	3250	6.8	4200	1.1
	Nb	3300	2.4		
	Mo	3300	3.7	4250	1.1
	W	3250	16	4000	3.1
He^+	Al			5200	100
	Cu	3250	0.8		
	Nb	3250	0.8		
	Mo	3500	3.0		
	W	3250	6.0		

beams of 2-mm diameter at the target surface. Projectile beam currents were monitored on a Faraday cup that could be periodically inserted into the beam line. Figure 1 gives a schematic view of the beam-target-monochromator geometry. Ambient pressures were maintained at 10^{-9} Torr in the target chamber using an ion pump. Targets were mechanically polished with 0.5-μm alumina and electropolished. Materials Research Corp. provided these metals with a purity of 99.97%.

The detection efficiency of the monochromator has been calibrated using a tungsten filament lamp as a standard of emission intensity. A lamp calibrated by the Eppley Laboratories according to the method of the National Bureau of Standards[12] was used as the primary standard for the visible spectrum. A Phillips tungsten filament lamp was used as the secondary standard because of its more convenient size. To extend the calibration to include ultraviolet wavelengths (3000–4000Å), the branching ratio method was employed.[13,14] Nitrogen gas was introduced into the target chamber and excited by a 25-keV beam of H^+ or He^+ ions. Observations were made of the relative signals from the second positive system of N_2 and the first negative system of N_2^+. Theoretical predictions of the relative intensities in these two spectral systems were obtained from the work of Thomas *et al.*[15] and Burns *et al.*[16] Hence, the relative sensitivity was established and could be normalized to the absolute sensitivity measured at visible wavelengths using the standard lamp. The monochromator detects only emissions perpendicular to the ion-beam direction. In estimating the number of photons produced per incident ion we have assumed that the emission is isotropic. The detection efficiency of the monochromator-detector system was calibrated to within ±50%.

For 25-keV H^+ impact energy, the observed spectra for Al, Mo, and Cu targets are given in Fig. 2. These spectra have been corrected for the transmission function of the monochromator-detector system and are on an absolute scale. With the exception of Al, we arbitrarily designate the band at 3250 Å, "band I" and the band at 4200 Å, "band II." Band I for Cu has been previously reported.[3] Our raw spectral data indicate that band I peaks at about 3250 Å, and the intensity drops sharply to 3000 Å. Unfortunately, it was impossible to perform precise calibrations of detection sensitivity at wavelengths below 3250 Å, and we have therefore omitted the lower-wavelength data from Fig. 2. Similar spectra were observed for He^+ ions incident on these same metals although band II was considerably reduced in such cases.

Spectra observed with targets of W, and Nb were similar to those of Cu and Mo in that band I was always present and very intense; band II was observed only with Cu, Mo, and W. Approximate estimates of emission intensity of these bands are given in Table I. The principal purpose of the table is to indicate that the aluminum emission is by far the most intense and is located primarily in the visible region; by contrast all other targets give essentially similar emission spectra with a peak at around 3250 Å.

It has been suggested[2] that the broadband emission observed under ion bombardment might be due to fluorescence of the window through which the target is observed; such fluorescence might be caused by secondary electrons, or reflected projectiles from the target, being incident on the window. Thus suggestion was tested by setting the optical system to view the window but not the target inside the vacuum system. With this configuration no emissions were observed; this test shows

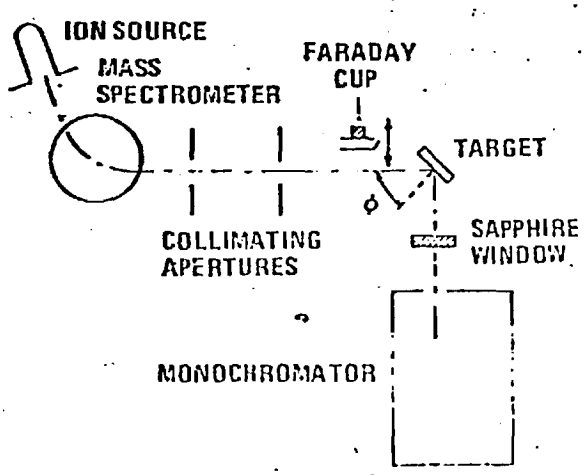


FIG. 1. Schematic diagram of the apparatus.

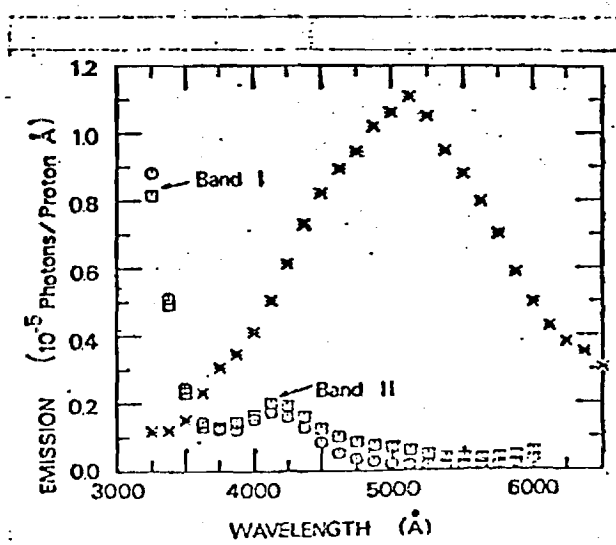


FIG. 2. Luminescence of Al, Mo, and Cu induced by 25-keV H^+ impact at an incidence angle ϕ of 45°. Stars, Al data; squares, Mo data (×25); circles, Cu data (×20).

:r that show some similarities with our spectra, irticularly in the strong emission of band I around 150 Å; there are considerable differences in de- il.

The similarity of the emissions observed from ı, Nb, Mo, and W targets suggests that the exci- tion mechanism is the same in all these cases id is probably not closely related to the detailed ınd structure of the solid. By contrast aluminum ıs a far more intense emission, different from e other metals studied. We shall offer no ex- anation of the emission from the noble and tran- tion metals and, with few exceptions, proceed to scuss only the rather intense characteristic nission of aluminum.

II. CHARACTERISTICS OF EMISSION FROM ALUMINUM

The impact of a 25-keV He^+ beam on an aluminum ırface gave a spectrum consisting primarily of ıe broad band shown in Fig. 2 but including also eak atomic lines of aluminum around 3089 and 956 Å; for H^+ impact the spectrum was the same ccept that the aluminum atomic lines were ab- ent.

There was concern that the emission might be elated to oxide layers on the surface and the fol- owing tests were made. For a new target bom- arded with He^+ for the first time the intensity of luminum lines from sputtered atoms decreased y a factor of 4 over an extended period of time. ombardment with Ar^+ caused a similar but more apid transient. Admitting oxygen at a pressure of 0^{-4} Torr to the target region caused the intensity the atomic lines to increase back to approxi- ıately the same level as observed with a new tar- et. A similar behavior has been observed else- here[20] during bombardment of Al by Ne^+ and is terpreted as being due to oxide formation.[20] We dopt that same explanation here. Following Kelly nd Kerkdijk[20] we believe that the constant inten- ity observed after prolonged bombardment indi- ates the removal of oxide and the formation of a lean atomic surface; exposure to O_2 causes re- ormation of an oxide layer. After the clean sur- ace condition was obtained the signal remained onstant indefinitely. Upon removing the beam or many hours and then recommencing bombard- ent there was again a short-term decay indi- ating some recontamination of the surface. For ll detailed measurements presented here the sur- ace was prebombarded with Ar^+ to attain what we elieve is an oxide-free surface. Some transient ffects were also observed in the intensity of the ontinuum spectrum. During initial bombardment f a new spot with He^+ ions the intensity of con- tinuum emission decreased by a factor of two. By contrast with sputtered atomic lines the intensity did not change on exposing the target to a pressure of 10^{-4} Torr of O_2, or removal of the beam for extended periods. Exposure of O_2 is known[20] to cause reformation of the oxide and we observe no change to the continuum; we therefore conclude that the continuum emission is not linked to oxide formation. The origin of the initial transient in continuum emission is not clear. We note, how- ever, that bombardment of aluminum by a 30-μA/cm^2 He^+ beam causes considerable damage to the surface that is clearly visible under a microscope. We suggest that the intensity of continuum emission is effected by this damage. In the following sections we shall postulate that emission is due to a radiative electron-hole recombination mechanism. Defect sites will certainly induce quenching of such luminescence by nonradiative recombination mechanisms as has been frequently observed in luminescence of alkali halides.[21] Our conclusion from these observations is that the surfaces were free of oxide contamination and that the luminescence of aluminum may be quenched by damage to the target.

As a further test for contaminants we examined the spectrum induced by Ar^+ on Al. The spectrum consisted only of aluminum lines and there was no evidence of CH bands that have been observed by others[22] and which indicates hydrocarbon contamination. Also there was no "blackening" of the surface; such blackening was seen by Kelly and Kerkdijk[20] when bombarding Al with low-beam currents of Ne^+ in a poor (10^{-6}-Torr) vacuum and was interpreted by them as carbon build up from impurity hydrocarbons.

We tested the dependence of the broad-band emission on the incident-ion current. The current was in fact altered by deflecting the beam by a square wave signal fed to a pair of condenser plates. The chopping frequency was 10 kHz and the duty cycle was altered to vary the beam current. The broad-band spectral shape was independent of the beam ϕ current and the intensity increased linearly with current up to the maximum current density available (30 μA/cm^2).

Studies were made of the broad-band shape as a function of projectile energy (10–30 keV) and projectile incidence angle on the surface ($\phi = 5°–70°$). No systematic changes to the spectral shape were observed.

Measurements were made of the intensity of the band emission as a function of the angle ϕ between the projectile beam and surface normal. Before starting detailed measurements the target was turned to the largest incidence angle ($\phi = 75°$) and the beam directed on the surface for an extended

me period until the signal was constant; this en-
ured that any transient effects due to sputter
eaning of the target were complete. Then the in-
nsity was monitored as a function of incidence
gle. Since we had already shown the shape of the
ectrum to be independent of incidence angle it
as satisfactory to monitor intensity only at a sin-
e wavelength. Figure 3 shows the measured in-
nsity as a function of the tangent of the incidence
gle. At the energy of which the data are taken
5 keV), the range of protons in aluminum is of
e order[23] 2000 Å; if the excitation events occur
roughout the projectiles range then the emission
ould occur throughout the 2000-Å path. How-
er, the absorption coefficient α for visible light
aluminum is of the order 10^6 cm^{-1}; thus in
actice the observer will detect only the emis-
ons occurring within approximately 100 Å of the
rface. The observed emission must therefore be
nfined to a relatively shallow region close to the
rface. It can be shown quite easily that with the
urces of emission localized close to the surface
a depth of the order α^{-1}, the observed intensity
ould vary as the tangent of the incidence angle
. Kerkdijk and Thomas[3] showed that the 3250-Å
nd induced by He^+ on copper (band I of Fig. 2)
d in fact vary in this manner. In Fig. 3 we show
line indicating a least squares fit of the data to
tangent function. Clearly the data does not follow
simple tangent function. The discrepancy may
ot be of great significance since our model is
ery simplistic and neglects such factors as inter-
al reflection of light at the surface, nonuniform

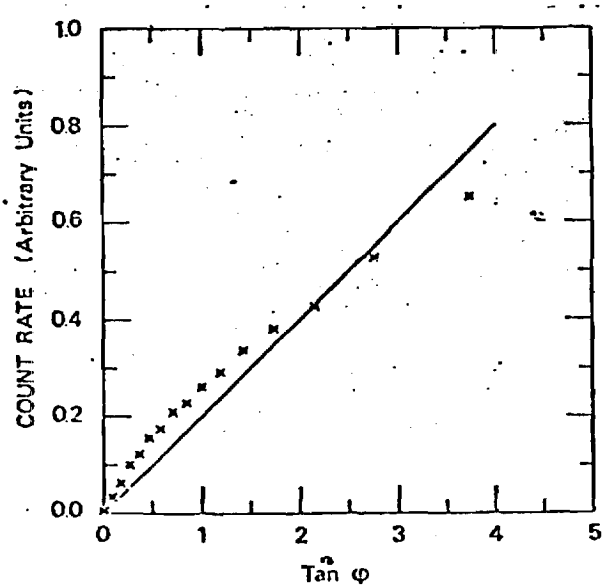


FIG. 3. Al emission, induced by 25-keV H^+ impact, t fixed wavelength 4750 Å, as a function of the tangent f the incidence angle ϕ. Stars, experimental data points; traight line, a least-squares fit of a tangent function to he data.

distribution of emitting sources, and influence of radiation damage on the optical properties of the solid. Moreover, we can use our previous backscattering computations[3] to show that at large incidence angles a substantial fraction of the projectiles are backscattered out of the surface; for an angle ϕ of 75° as much as 20% of the incident 25-keV proton flux will in fact backscatter out of the surface. Thus the dissagreement, indicated in Fig. 3 between experiment and the simplistic model, is not at all surprising.

The total intensity in the aluminum band was determined using the absolute calibration of sensitivity and integrating the emission spectrum between 3250 and 6500 Å. The emission from the surface was assumed to be isotropic. For 25-keV H^+ on the aluminum target we determine an emission into all directions of 0.02 ± 0.01 photons per incident ion. The limit of error specified represents the absolute reproducibility of our data. An estimate of the relative reproducibility of our data is ±5%. A 25-keV ion will lose some kiloelectronvolts of energy in the approximately 100-Å depth from which radiation can escape. Thus, only a small fraction of the energy deposited in the solid is in fact used in the formation of excited states.

We did attempt to observe polarization of the emission using a simple polaroid analyzer. Certain of the mechanisms we shall examine as possible sources of the emission are expected to exhibit strong polarization with respect to the direction of the projectile beam. No significant polarization was observed for any angle of projectile incidence on the surface.

IV. POSSIBLE EMISSION MECHANISMS

The various tests detailed previously confirm that the broad band emission is not an artifact of the experimental arrangement. The emission has its origin in the target surface and is excited by the incident projectile. This conclusion holds for all the metal targets studied. Various possible mechanisms were considered as the source of the broad-band emission, and we discuss here those that were not consistent with our observations.

Boersch *et al.*[24] have considered the possibility that broad-band light emission induced by electron impact on solids is due to bremsstrahlung or transition radiation. Goldsmith and Jelley[25] have in fact observed transition radiation as protons with MeV energies collide with metal targets. These two mechanisms are well understood, and Boersch *et al.* give equations from which the intensity of emission can be computed. Using these formulations for the case of 25-keV H^+ incident on a metal target at 45° to the surface normal, we predict

that the emission due to either bremsstrahlung or to transition radiation should be of the order 10^{-12} photons per incident proton emitted in a wavelength interval of 1 Å into a solid angle of one steradian. This is some seven orders of magnitude smaller than the intensities we observe. Moreover, both Bremsstrahlung and transition radiation should be strongly polarized whereas our observed emissions are not polarized.

We conclude that neither of these mechanisms provides a significant contribution to our observed emission.

High-energy electron impact on metals produces broad band emission structure that has been identified as a decay of the surface plasmon. Boersch *et al.*[24] claim that electron impact on silver yields the radiative decay of surface plasmons. For the case of unoxidized aluminum the surface plasmon has an energy of 10.3 eV. For an oxidized surface, this energy is lowered to 7 eV (1770Å). On the basis of the location of the Al band emission (4750 Å), the surface plasmon model was discarded. Also in the case of the other metals studied here (Cu, Mo, W, and Nb) the surface plasmon energy does not correspond to the position of the principal emission peak (3250 Å).

On the basis of the above arguments it is considered that the emissions observed here are not attributable to Bremsstrahlung, transition radiation, nor to decay of plasmons.

The emission from the aluminum target has a rather different spectral distribution from that of the other metals considered; moreover it is at least one order of magnitude more intense. We propose that the emission from aluminum is due to an electron-hole recombination mechanism; the initial excitation being provided by the interaction of the projectile with valence electrons. Bonnot *et al.*[8] have previously invoked a recombination mechanism to explain cathodoluminescence in copper, although they make no attempt to predict the spectrum in detail. In Sec. V we discuss certain of the optical properties of aluminum and develop an approximate prediction of the spectrum expected from electron hole recombination. We offer no further attempts to explain the emissions from Cu, Mo, W, and Nb targets.

V. OPTICAL PROPERTIES OF ALUMINUM

A. Definition of terms

The objective here is to consider two models for the band emission of Al. Detailed agreement with experiment is not sought. The Fermi distribution function is not handled self-consistently, and details of the excitation process are not considered. The distribution function $n(\vec{k})$, with $\vec{k}$ a wavelength in reciprocal space, is somehow different from the equilibrium distribution since carriers (electrons and holes) are generated continuously by collisions of the projectile with the target; this is a nonthermal process.[25] Self-consistency (fixed concentration of electrons) can be obtained by the introduction of a quasi-Fermi level; in our calculations we do not impose this self-consistency, since we mainly seek only quantitative agreement with the energy location of structure. The following definitions are introduced, to facilitate discussion of the models. Direct (vertical) interband transitions involve initial and final states which lie at the same point (wave vector $\vec{k}$) in the first Brillouin zone (reduced zone scheme).[27,28] If $E_i(\vec{k})$ and $E_f(\vec{k})$ are the energies of the initial band i and final band f, respectively, then in optical absorption at photon energy $E=\hbar\omega$ the locus of all points which satisfy

$$E_f(\vec{k})-E_i(\vec{k})=E \qquad (1)$$

defines a surface of constant interband energy difference (the optical band). The joint density of states (JDOS) per unit volume is defined by

$$J(E)=\frac{2}{(2\pi)^3}\sum_{i,f}\int'_{BZ} d^3k\,\delta[E_f(\vec{k})-E_i(\vec{k})-E], \qquad (2)$$

where the prime denotes that the integration is to be performed only over regions of $\vec{k}$ space in which $E_f>E_F\geq E_i$, where E_F is the Fermi energy (BZ denotes Brillouin zone). Since the summation is performed over all band pairs, the JDOS represents the total number of direct transitions which can contribute to the optical absorption at photon energy E. The properties of the energy conserving Dirac delta function allow the reduction of Eq. (2) to the familiar surface integral

$$J(E)=\frac{2}{(2\pi)^3}\sum_{i,f}\int'_{BZ}\frac{dS_{\vec{k}}}{|\nabla_{\vec{k}}(E_f-E_i)|}, \qquad (3)$$

the integration being done over the sets of surfaces defined by Eq. (1).

In a similar way, we define quantities for optical emission due to electron-hole recombination. The absolute meaning of the similar quantities is that we are neglecting the thermalization (rising of holes and falling of electrons due to phonon emission) of the excess carrier distribution generated by ion impact. We assume this to be a small frozen distribution in excess of the equilibrium distribution and that the Fermi level is unperturbed. We have by definition at wave vector $\vec{k}$

$$E_i(\vec{k})-E_f(\vec{k})=E, \qquad (4)$$

where $E=\hbar\omega$ is the emission photon energy. Again, $E_i(\vec{k})$ is the initial band energy and $E_f(\vec{k})$ is the final band energy. Here the upper band state $\vec{k}_i$ is

ccupied, the lower-band state $\vec{k}_f$ is unoccupied:

$$J(E)=\frac{2}{(2\pi)^3}\sum_{i,f}\int_{BZ}^{*}d^3k\,\delta[E_i(\vec{k})-E_f(\vec{k})-E]. \quad (5)$$

he disposition of the initial and final band energies relative to the Fermi level will be designated hen we discuss particular models. Again, this educes to a surface integral

$$J(E)=\frac{2}{(2\pi)^3}\sum_{i,f}\int_{BZ}^{*}dS_{\vec{k}}/|\nabla_{\vec{k}}(E_i-E_f)|, \quad (6)$$

ne integration being carried out over the sets of urfaces defined by Eq. (4).

The JDOS for absorption suffices to account for nuch of the structure in the complex part of the ielectric constant ϵ_2 in semiconductors.[29] However, much of the oscillator strength of Al is exausted by structurepoor interband absorption so hat it becomes necessary to include the relevant natrix elements to provide a truly satisfactory xplanation of the interband absorption. However, ne can sometimes anticipate the photonenergy ocation of structure in simple metals, using farrison's parallel-band model.[30]

In what follows we shall first discuss the calculation of energy band structure and wave functions or aluminum. We shall then test the adequacy of he computed band structure by calculating the conventional electron density of states which may e compared with previous predictions. In predicting the recombination rate one must also include the relevant matrix elements; to ensure the adequacy of the values used, we have also calculated the complex part of the dielectric constant ϵ_2; again this is compared with previous calculations. Finally, we utilize a development of Eq. (6) including the relevant matrix elements to predict a spontaneous recombination rate.

B. Band structure of aluminum

To generate the energy band structure and wave functions an empirical pseudopotential model with four orthogonalized plane waves was employed.[27] Ashcroft's[10] local pseudopotential coefficients $V_{\vec{G}}$, defined via

$$V_P(\vec{r})=\sum_{\vec{G}}V_{\vec{G}}e^{i\vec{G}\cdot\vec{r}}=V_{111}e^{i\vec{G}_{111}\cdot\vec{r}}+V_{11\bar{1}}e^{i\vec{G}_{11\bar{1}}\cdot\vec{r}}+V_{200}e^{i\vec{G}_{200}\cdot\vec{r}}, \quad (7)$$

where $V_{11\bar{1}}=V_{111}=0.2435$ eV and $V_{200}=0.7646$ eV were used together with the free electron mass and the lattice constant[31] $a=4.04145$ Å. Reciprocal-lattice vectors $\vec{G}$ are in units of $2\pi/a=1$; e.g. $\{(2\pi/a),(2\pi/a),(2\pi/a)\}$ is written (1, 1, 1). We worked within Ashcroft's[10] choice of the $\frac{1}{48}$th symmetry sector of the Brillouin zone. In units of $\hbar^2/2m=1$ and $2\pi/a=1$, the secular determinant for the one-electron pseudo wave equation, formally, took a simple form

$$\begin{vmatrix} \vec{k}^2-E_{\vec{k}} & V_{111} & V_{111} & V_{200} \\ V_{111} & [\vec{k}-(1,1,1)]^2-E_{\vec{k}} & V_{200} & V_{111} \\ V_{111} & V_{200} & [\vec{k}-(1,1,\bar{1})]^2-E_{\vec{k}} & V_{111} \\ V_{200} & V_{111} & V_{111} & [\vec{k}-(2,0,0)]^2-E_{\vec{k}} \end{vmatrix}=0, \quad (8)$$

when the pseudo wave function was expanded

$$\phi_{\vec{k}}(r)=a_{\vec{k}}e^{i\vec{k}\cdot\vec{r}}+a_{\vec{k}-(1,1,1)}e^{i[\vec{k}-(1,1,1)]\cdot\vec{r}}+a_{\vec{k}-(1,1,\bar{1})}e^{i[\vec{k}-(1,1,\bar{1})]\cdot\vec{r}}+a_{\vec{k}-(2,0,0)}e^{i[\vec{k}-(2,0,0)]\cdot\vec{r}}. \quad (9)$$

Now through the definitions

$$\begin{aligned} T_1&=\vec{k}^2-E_{\vec{k}},\\ T_2&=[\vec{k}-(1,1,1)]^2-E_{\vec{k}},\\ T_3&=[\vec{k}-(1,1,\bar{1})]^2-E_{\vec{k}},\\ T_4&=[\vec{k}-(2,0,0)]^2-E_{\vec{k}} \end{aligned} \quad (10)$$

the secular determinant was expanded and cast into the form

$$(T_1T_4-V_{200}^2)(T_2T_3-V_{200}^2)-V_{111}^2\times(T_1+T_4-2V_{200})(T_2+T_3-2V_{200})=0. \quad (11)$$

At the choice of symmetry points given in Table II, two or more kinetic-energy terms T_i of Eq. (11) became equal. Some or all of the roots were then found by factoring. The results for the W point were conventional. We believe the results for the other symmetry points are somewhat original. Obviously the energy gaps differ somewhat from the standard two-band predictions (e.g. at the L point: $E_{12}=E_{34}=2V_{111}$ and at the X point: $E_{12}=E_{34}=2V_{200}$ in the two-band model). We hope these analytical results for this popular four-band model prove useful to future workers who seek checks on their numerical procedures.

The transformation which diagonalized the Hamonian matrix to produce the eigenvalues also deied the pseudo wave functions. These were subquently used to evaluate the matrix elements to Introduced below. Division of the ΓX line into 4 equal segments defined the linear step size ıich divided the entire volume of the $\frac{1}{48}$th symetry sector into a cubic mesh of 538 385 points. ıen careful use was made of the number of like ctors, we obtained the equivalent of four-band ergies at exactly 24 612 968 points throughout e Brillouin zone.

The energy band structure for a number of mmetry lines and other lines are presented as appendix in both graphical and tabular form. ıe new zero of energy was chosen to be the botm of the first band, and the Fermi level was ven by Ashcroft.[10] We number band indices 1–4 order of increasing energy for a given wave ctor $\vec{k}$; in this way, bands do not cross. These nds given in the Appendix provide a somewhat ore extensive presentation of energy levels than eceding work such as that by Ashcroft[10]; however, the present results are in complete agreeent with the preceding work wherever comparin is possible.

C. Numerical procedures and density of states

To provide a check on the accuracy of the band ructure, we generated in a conventional manner e electron density of states (DOS) per unit volne using the form [see Eqs. (2)–(6)]

$$D(E)=\frac{2}{(2\pi)^3}\sum_j \int_{BZ} d^3k\,\delta[E_j(\vec{k})-E]. \tag{12}$$

In calculations of any of these density functions (and similar integrals below) it is simplest to work directly with the volume integrals which contain the Dirac delta energy conserver. With judicious interpretation, the Dirac delta became a Kronecker delta. We rewrote Eq. (12) as

$$D(E_m)=\frac{2}{(2\pi)^3}\frac{(\Delta k)^3}{\Delta E}\sum_{\vec{k}} L V_{\vec{k}} \times \sum_{j=1}^{4}\Delta\left(E_m-\frac{\Delta E}{2},\ E_j(\vec{k}),\ E_m+\frac{\Delta E}{2}\right) \tag{13}$$

with

$$\Delta\left(E_m-\frac{\Delta E}{2},\ E_j,\ E_m+\frac{\Delta E}{2}\right)=\begin{cases}0, & |E_j-E_m|>\frac{\Delta E}{2},\\ 1, & |E_j-E_m|\leq\frac{\Delta E}{2}.\end{cases}$$

The number of vectors equivalent to those within the symmetry sector were incorporated in the "like vector" $LV_{\vec{k}}$ term.[32] The sum over $\vec{k}$ was restricted to this sector. In the generation of the band structure, each of the 538 385 $\vec{k}$ vectors, the number of like vectors, the four eigenvalues, and the four wave functions were calculated and stored on magnetic tape. We then evaluated the contribution to the DOS at a given electron "bin" energy E_m of width $\Delta E=0.1$ eV. Histograms were gen-

TABLE II. Exact eigenvalues[a] of 4-band secular determinant for fcc crystals at various symmetry points. Vertical interband gap energies are likewise exactly given by $E_g=E_i(\vec{k})-E_j(\vec{k})$. Note that the E values are the empty lattice ($V_{\vec{G}}=0$) eigenvalues ($E=\hbar^2\vec{k}^2/2m$) at the respective points; a blank or approximate entry corresponds to an irreducible cubic polynomial. For simplifying the display of this table we have written V_1 for V_{111} and V_2 for V_{200}; the symbols A, B, and C are defined as follows:

$$A=\tfrac{1}{2}[(\tfrac{8}{3}E_L)^2+4(V_2-V_1)^2]^{1/2},$$
$$B=\tfrac{1}{2}[(\tfrac{8}{3}E_L)^2+4(V_2+V_1)^2]^{1/2},$$
$$C=\tfrac{1}{2}[E_X^2+(4V_1)^2]^{1/2}.$$

BSW symbol[b]	$\vec{k}$	Band 1	Band 2	Band 3	Band 4
Γ	(0,0,0)	≈ 0	$4E_L-V_2$	$\approx 4E_L+V_2$	$\approx 4E_X$
L	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$(\frac{7}{3}E_L-V_1)-A$	$(\frac{7}{3}E_L+V_1)-B$	$(\frac{7}{3}E_L-V_1)+A$	$(\frac{7}{3}E_L+V_1)+B$
X	(1,0,0)	E_X-V_2	$(\frac{3}{7}E_X+V_2)-C$	$2E_X-V_2$	$(\frac{3}{7}E_X+V_2)+C$
U	$(1,\frac{1}{4},\frac{1}{4})$	E_U-V_2			
W	$(1,\frac{1}{2},0)$	E_W-V_2	E_W-V_2	$E_W+V_2-2V_1$	$E_W+V_2+2V_1$

[a] Eigenvalue entries are given relative to the empty lattice choice of energy zero.
[b] According to the notation of L. P. Bouckaert, R. Smoluchowski, and E. Wigner [Phys. Rev. 50, 58 (1936)].

erated from the contents of the bins, after all $\vec{k}$ vectors has been sampled.

The absolute value of the DOS is given in Fig. 4. Similar structure in the range of the Fermi level has also been reported by others.[11,33] This departure from an $E^{1/2}$ dependence reflects the departure of the free-electron bands from parabolocity, upon contact with the zone boundaries. The tailing off of the DOS at ~19 eV means that the four-band model is running out of electrons.

A bonus of this check on our numerical procedures was that it also gave a measure of the self-consistency of Ashcroft's[10] pseudopotential model far away from the Fermi surface. It should be noted that Ashcroft obtained his Fermi level by adjusting the highest energy level of occupancy until $\frac{3}{2}$ the volume of the Brillouin zone was filled. Since the fcc conventional cell of Al had four atoms, each contributing three electrons to these valence bands, we found the electron density

$$\rho = N/V = 12/a^3 = 1.818\times10^{23}\ \text{electrons/cm}^3, \tag{14}$$

with $a = 4.041\,45$ Å, as a basis with which to compare the results for electron concentration

$$\rho(E_F) = \frac{N}{V}(E_F) = \int_0^{E_F} D(E)\,dE \tag{15}$$

for successive values of E_F. We obtained the results given in Table III. This table gives a Fermi level, by comparison with Eq. (14), of 11.7 eV. Now Ashcroft obtained the value 11.647 eV. When we recall that our energy bins E_m were of width 0.1 eV, we find the agreement admirable. This calculation provides further confirmation of the utility of this pseudopotential, away from the Fermi level.

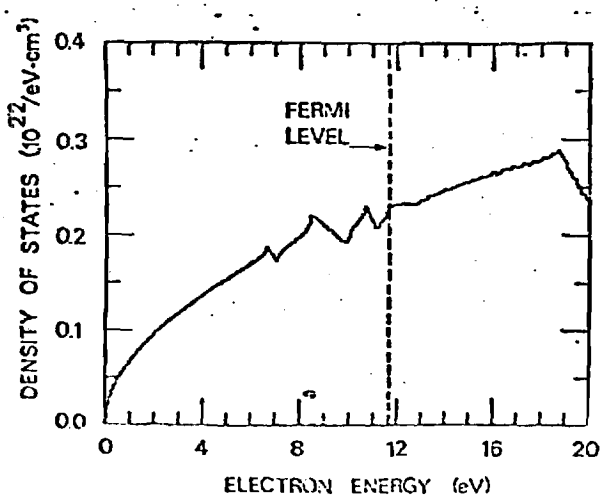


FIG. 4. Electron density of states (DOS) for Al in absolute units.

D. Interband contribution to ϵ_2

The next stage of our computation was the generation of the interband contribution to ϵ_2. This was designed to provide the ultimate test of our procedures, since the DOS calculation only involved the eigenvalues. Our choice of energy bin width allowed a ready comparison of this four-band model with the nine-band model of Brust,[11] who used a similar energy step.

The interband contribution to ϵ_2 is given by the standard result[34] for isotropic crystals

$$\epsilon_2(E) = \frac{4\pi^2e^2\hbar^2}{3m^2E^2}\frac{2}{(2\pi)^3} \times \sum_{i,f}\int_{BZ} d^3k\,|M_{if}(\vec{k})|^2\,\delta[E_f(\vec{k}) - E_i(\vec{k}) - E], \tag{16}$$

where $E = \hbar\omega$ and all similar terms have the same meaning as in the definition of the JDOS for absorption in Eq. (2). The essentially new term is $|M_{if}(\vec{k})|^2 = |\langle U_{\vec{k},f}|\nabla|U_{\vec{k},i}\rangle|^2$, where $U_{\vec{k},f}$ and $U_{\vec{k},i}$ represent the Bloch functions. These Bloch functions are obtained by factoring Eq. (9) in the form $\phi_{\vec{k}}(\vec{r}) \equiv U_{\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$ so that immediately

$$U_{\vec{k}}(\vec{r}) = a_{\vec{k}} + a_{\vec{k}-(1,1,1)}e^{-i(1,1,1)\cdot\vec{r}} + a_{\vec{k}-(1,1,\bar{1})}e^{-i(1,1,\bar{1})\cdot\vec{r}} + a_{\vec{k}-(2,0,0)}e^{-i(2,0,0)\cdot\vec{r}} \tag{17}$$

Note that Eq. (16) is in fact the JDOS if we ignore the terms $|M_{if}(\vec{k})|^2$ and $4\pi^2e^2\hbar^2/3m^2E^2$. In many semiconductors, this matrix element can be treated as a constant. It follows that a knowledge of the JDOS accounts for the structure of ϵ_2. In simple metals, however, this matrix element is a strong function of $\vec{k}$.

As in Eq. (3), we cast ϵ_2 into a form convenient for calculation.[35] This led to

TABLE III. Evaluation of the Fermi Level E_F, by trial integration of the DOS to give electron density ρ. From the known lattice constant, we have $\rho = 1.818\times10^{23}$/cm^3 as a base for comparison.

Trial E_F (eV)	$\rho(E_F)$ (10^{23} electrons/cm^3)
11.5	1.7699
11.6	1.7922
11.7	1.8151
11.8	1.8380
11.9	1.8612

$$\epsilon_2(E_m)=\frac{1}{3}\frac{e^2\hbar^2}{\pi m^2 E_m^2}\frac{(\Delta k)^3}{\Delta E}\sum_{\bar{k}}{}' LV_{\bar{k}}\sum_{i,f}|M_{if}(\bar{k})|^2\,\delta\left(E_m-\frac{\Delta E}{2},E_f(\bar{k})-E_i(\bar{k}),E_m+\frac{\Delta E}{2}\right), \quad (18)$$

th

$$\Delta\left(E_m-\frac{\Delta E}{2},E_f-E_i,E_m+\frac{\Delta E}{2}\right)=\begin{cases}0, & |E_f-E_i-E_m|>\dfrac{\Delta E}{2},\\ 1, & |E_f-E_i-E_m|\leq\dfrac{\Delta E}{2}.\end{cases}$$

The procedure for constructing the histogram ϵ_2 followed the steps taken in constructing the OS, with the following exceptions: the addition the momentum matrix element, the double sum er band indices, and the primed sum over $\bar{k}$ (as fore, the prime denoted $E_f > E_F \geq E_i$). The re-lts for ϵ_2 are presented in Fig. (5). For com-rison, Brust's nine-band model results are otted on the same scale. The agreement at the 5-eV structure is fair. Presumably the source the disagreement is due to "convergence" er-rs. At several symmetry points Brust used a 5-band model to evaluate more accurate bands an the nine-band results. The four- and nine-nd results did not "converge" to these best nds, and the differences between the four- and ne-band results were sometimes ~0.2 eV. By contrast, the agreement at the 1.5 eV struc-re is excellent. Apparently the convergence rors represent a lesser relative part of the en-gy differences at the higher-photon energy nge. The comparison of this type of calculation th ϵ_2 spectra generated from reflectance mea-rements has been carried out at length.[11,35-38] ffice it to say here that these results accounted r the experimental ϵ_2 spectra nicely.

Two features were of immediate interest. First, could proceed with a very similar calculation r the spontaneous recombination rate in Al, with nfidence that our band structure (eigenvalues d eigenfunctions) was properly assembled. cond, the parallel-band model and these full lculations assure interband structure at V_{111}(0.5 eV) and ~$2V_{200}$(1.5 eV) for photon ab-rption. The proposition we confronted was ether or not this full (full meaning matrix ele-ents included) calculation for photon emission ould lead to structure other than that predicted mply on the basis of parallel bands (the parallel nd model is based on JDOS argument, which is ver entirely satisfactory in the case of metals).

E. Spontaneous recombination rate–Model I

The direct recombination we envisaged, involved electron making a downward vertical transition om a band below the Fermi level to a hole, gen-erated by ion impact further down. Here we did not consider the recombination due to excited electrons falling from states above the Fermi level; a second model discussed in Sec. V F in-volves an excited band.

We rewrote the primed integral for the JDOS for emission, Eq. (5), in the form

$$J(E)=\frac{2}{(2\pi)^3}\sum_{i,f}\int_{BZ}d^3k\,\mathcal{F}_i(1-\mathcal{F}_f)\times\delta[E_i(\bar{k})-E_f(\bar{k})-E], \quad (19)$$

where at thermal equilibrium $\mathcal{F}_i$ was the Fermi distribution function, $\mathcal{F}_i=(1+e^{(E_i-\mathcal{E})/KT})^{-1}$. Under charged-particle bombardment or photoexcitation, this distribution function $\mathcal{F}(E)$ departed from thermal equilibrium and the JDOS obtained a finite value for metals [$J(E)$ vanishes at thermal equilib-rium since $1-\mathcal{F}(E_f)=0$, when $E_F \geq E_i > E_f$ unless the temperature is exceeding high].

With these notions, we wrote the spontaneous electron-hole recombination rate due to direct transitions[25,39,40] as

$$r(E)\propto E\sum_{i,f}\int_{BZ}d^3k|M_{if}(\bar{k})|^2\times\mathcal{F}_i(1-\mathcal{F}_f)\delta[E_i(\bar{k})-E_f(\bar{k})-E]. \quad (20)$$

This expression gave the rate at which photons of energy $E=\hbar\omega$ were emitted per unit energy inter-val $dE=\hbar d\omega$. We let the following distribution function describe the perturbed metal:

$$\mathcal{F}_i=\begin{cases}0, & E_i>E_F,\\ 1, & E_i\leq E_F,\end{cases} \quad (21)$$

$$\mathcal{F}_f=\sigma, \quad E_f<E_F.$$

This σ was assumed to be a small arbitrary con-stant. That is, the generated holes were frozen, and the supply of electrons for recombination came entirely from the two conduction bands in Al (bands 2 and 3).

The emission rate was rewritten in a form con-venient for computation. This led to

$$r(E_m) \propto E_m \frac{(\Delta k)^3}{\Delta E} \sum_{\vec{k}}{}' L V_{\vec{k}} \sum_{ij} |M_{ij}(\vec{k})|^2 \Delta\left(E_m - \frac{\Delta E}{2}, E_i(\vec{k}) - E_f(\vec{k}), E_m + \frac{\Delta E}{2}\right), \quad (22)$$

with

$$\Delta\left(E_m - \frac{\Delta E}{2}, E_i - E_f, E_m + \frac{\Delta E}{2}\right) = \begin{cases} 0, & |E_i - E_f - E| > \frac{\Delta E}{2}, \\ 1, & |E_i - E_f - E| \leq \frac{\Delta E}{2}. \end{cases}$$

The histogram for the emission rate was constructed by the procedure established above. This mission rate is given in Fig. 6. Most striking is he similarity to the ϵ_2 histogram of Fig. 5. gain, the strongest structure occurred at $2V_{111}$(0.5 eV) and ~$2V_{200}$(1.5 eV). A parallel-band nodel was relevant to this proposed recombination nodel. The energy band structure in the Appendix llustrates tracking at nearly parallel bands along UW and XW($2V_{200} \approx 1.5$ eV). We also found nearly arallel bands along LK and LU($2V_{111} \approx 0.5$ eV).

The surface integral for the JDOS for emission, q. (6), accounted for the large contributions to he emission rate on these X and L zone faces:[1] Ve focused our attention of the denominator of Eq. 6) and saw that nearly parallel bands made anomlously large contributions to this integral. Thus, he optical properties for emission should be simlar to those for absorption, in so far as the hoton-energy location of strong structure is conerned. Apart from this symmetry between absorption and emission, we found no other structure of interest. We believed there was no *a priori* reason to preclude the possibility of other structure, since the $\vec{k}$ dependence of the matrix elements was so strong. This symmetry may hold for all simple metals.

We see that within this recombination picture there were two conduction bands which could readily fill generated holes (the fourth band lies above the Fermi level). In Mooradian's picture for the electron-hole recombination in Cu, electrons fell from the upper part of the conduction band to generated holes in d bands vertically below. An idea of the relative weight of the contribution of these two conduction bands in Al to the recombination process can be seen from the Fig. 7. These are our computed intersections of the Fermi surface with the (110) plane and are similar to those generated by Harrison.[27] Occupied states are uniformly located between the zone boundaries and the Fermi surface. This geometrical construction of the number of occupied states in these two bands (second and third) agreed with our re-

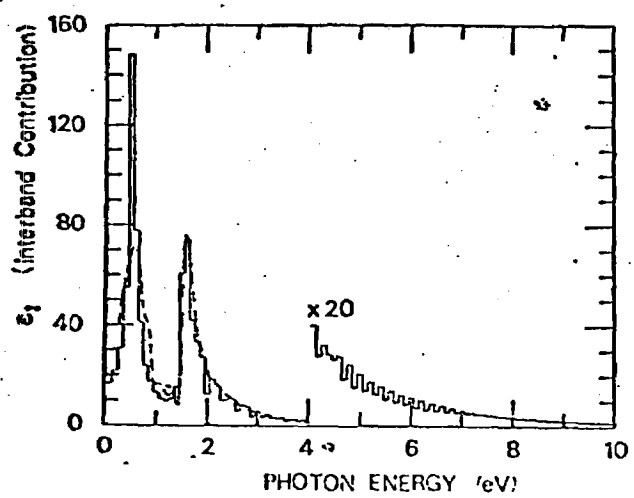


FIG. 5. Interband contribution to the complex part of the dielectric constant ϵ_2. Histogram, present 4-band results; smooth curve, 9-band model of Brust. (The smooth curve was generated for the sake of illustration. It fits Brust's result exactly at his reported energy steps, which are similar to ours.)

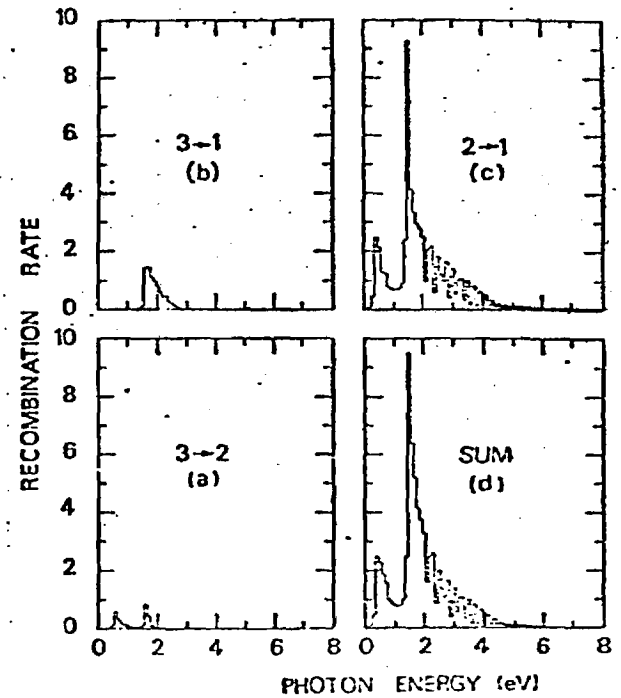


FIG. 6. Computed recombination rate (photons/sec eV, arbitrary units) according to Model I. Individual band-pair contributions are illustrated (a) 3—2, (b) 3—1, (c) 2—1. The histogram (d) is the sum of (a), (b), and (c).

lt below that the lower-conduction band (band 2) eracts more strongly with the first band. The ıtribution to the JDOS of band pairs 2, 1 far ceeds the contributions of band pairs 3, 2 and nd pairs 3, 1.

F. Spontaneous recombination rate—Model II

Ve now introduce the second model based on ect interband recombination. This model is nilar to the established picture[9] of luminescence rived from semiconductors and insulators. In- ection of the Al band structure (see the Appen-) shows that there is an excited band (band 4) ich has a minimum at a critical point [at a tical point, we have $\nabla_{\vec{k}} E_i(\vec{k}) = 0$]. This mini- m occurs at the W point (there are 24 equiva- t W points in the first Brillouin zone). The stence of a minimum in an excited band ensures t a "localized" supply of electrons will be available, under excitation, to fill vacancies generated below (this is a localization in reciprocal space). Any electron which is excited from band 1, 2, or 3 to band 4 may reach the W point via phonon emission. Further decay can only be radiative, since the minimum at W is energetically isolated from the other bands.

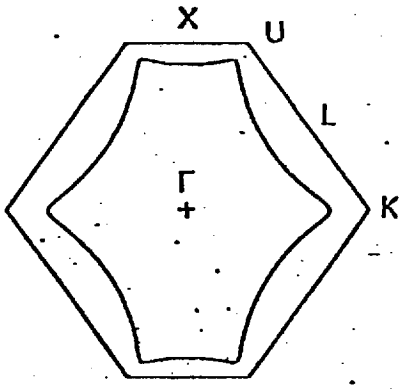
In the spirit of the present calculations, we arbitrarily let the 4th band be occupied up to 0.5 eV above the minimum at the W point. Again we assumed the generated holes were isotropically distributed. The following distribution function described the perturbed metal:

$$\mathfrak{F}_i = \begin{cases} 1, & (E_{4,\min} + 0.5\ \text{eV}) \geq E_4 \geq E_{4,\min}, \\ 0, & E_4 > (E_{4,\min} + 0.5\ \text{eV}), \end{cases} \qquad (23)$$

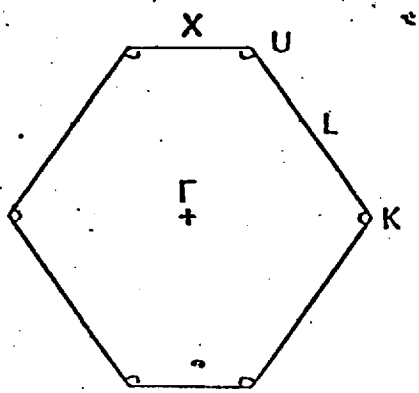
$$\mathfrak{F}_f = \sigma, \quad E_f \leq E_F .$$

This σ was an arbitrary constant, as above. Only band 4 was used as a source of initial states. $E_{4,\min}$ denoted the band minimum. The emission rate was computed from an expression identical to Eq. (22) except that the Kronecker delta was made consistent with Eq. (23). The resulting histogram is presented in Fig. 8. In the spectral ranges of interest, we have band pairs 4, 2 giving rise to the dominant peak at ~1.8 eV, and band pairs 4, 1 giving rise to a weak shoulder at ~2.8 eV.

SECOND BAND INTERSECTION



THIRD BAND INTERSECTION



IG. 7. Intersections of the Al Fermi surface with the) plane. (The first band is fully occupied, and the th band is empty at thermal equilibrium.) Occupied es lie between the curves and the zone edges. See Appendix for the band structure.

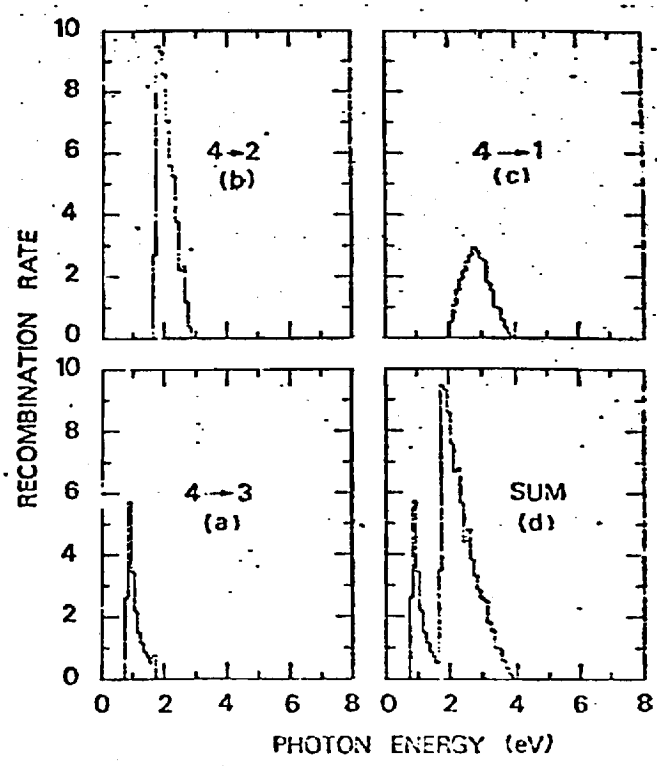


FIG. 8. Computed recombination rate (photons/sec-dV, arbitrary units) according to Model II. Individual band-pair contributions are illustrated (a) 4→3, (b) 4→2, (c) 4→1. This histogram (d) is the sum of (a), (b), and (c).

V. COMPARISON OF THEORY AND EXPERIMENT

The results of the two models for the spontaneous recombination rate are quite different (Fig. 6 and 8). Model I predicts an emission spectrum similar to the ϵ_2 spectrum, with structure at 0.5 and 1.5 eV. Model II gives rise to rather different structure at higher energies, 1.8 and 2.8 eV. Both these models are illustrated in Fig. 9, along with the experimental emission for Al. It should be noted that only the experimental data is absolute; both predicted curves are relative and their absolute magnitudes have been fixed to facilitate comparison with experiment.

We regard the degree of correspondence between experiment and Model II as encouraging. Our overall objective has been to determine whether the electron-hole radiative recombination process is a plausible explanation of the observed emission. As such, the important question is whether the model predicts emission at the wavelengths where we observe it; clearly the model does this. One of the major inadequacies of the computation is that we have assumed the electron-hole pairs to be uniformly distributed throughout the available bands; this assumption also means that we essentially ignore all details of the collisional excitation process. We could force better agreement between theory and experiment by adopting suitable excitation distribution functions so that the shape of the predicted intensity distribution agrees better with experiment. One cannot expect detailed agreement of theory and experiment until the physics of the collision mechanism is included. The calculation predicts that the maximum of intensity due to recombination of band 4 with 2 should lie at 1.8 eV and the maximum for recombination of band 4 with 1 should lie at 2.8 eV (see Fig. 8). The maximum in the experimentally measured emission occurs at 2.4 (point *A* in Fig. 9) and there is a weak shoulder at 3.3 eV (point *B* in Fig. 9); the experimental data thus shows two features but shifted from the predicted energies by about 0.5 eV. The major intensity contributions to the experimentally observed band lie at photon energies where the predicted intensity is also large.

There seems to be little correspondence between the experiment and the calculations by model I. The predicted peak is at 1.5 eV, quite significantly removed from the experimental peak *A* at 2.3 eV. More important, the observed intensities are most significant at photon energies where the predicted intensities are 5% or less of the maximum. Thus, the first model does not clearly satisfy our basic criterion of predicting the range of photon energies where the greatest intensities are observed.

We would emphasize that the radiative recombination mechanism can be occurring in only a relatively small proportion of the excitation events. An incoming projectile loses some keV of energy in the first 100 Å or so of target from which radiation can escape; this energy must be lost principally to collisions with electrons. Our observed emission represents only about 0.02 photons per incident ion, with an average photon energy of 2.4 eV. Thus, the energy emitted as radiation represents only one part in 10^5 of the energy lost by the projectile in collisions with electrons. Radiative recombination is a rather rare event.

In conclusion then, we have established that an electron-hole recombination mechanism can plausibly explain the broad-band emission when light projectiles strike aluminum. It would appear that the recombination occurs between electrons in the excited band 4 with generated vacancies below. The mechanism is similar to that invoked to explain luminescence in materials other than metals. Close comparison between theory and experiment is probably not warranted until the details of the initial collisional excitation process can be included.

APPENDIX

In performing the calculations discussed in the body of the paper, it was necessary to generate the band structure of aluminum. Previous calculations of band structure generally present graphically, energies along symmetry lines and on zone

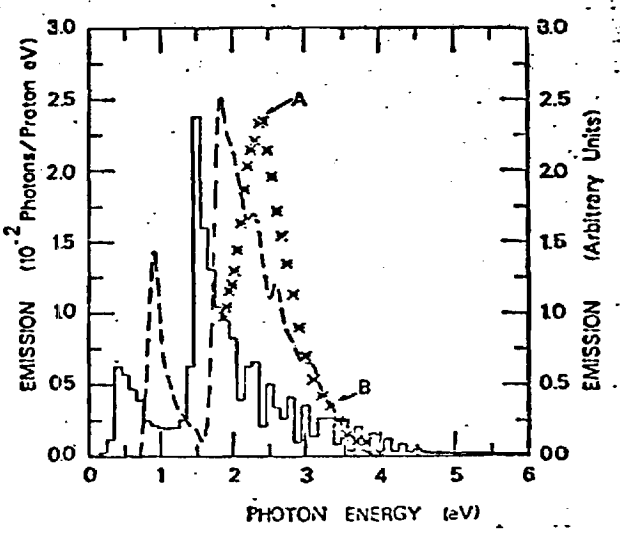


FIG. 9. Theoretical emissive rates according to Models I and II (arbitrary units) compared with the absolute value of the experimental emission. Histogram, Model I; dashed curve, Model II; stars, experimental emission. (For illustration here, the histogram for Model II, shown in Fig. 8, has been computer-fit with a dashed curve.)

ABLE IV. The $E_i(\vec{k})$ vs $\vec{k}$, for band indices $i=1$ through 4, are listed. The first column gives the BSW symbol, re appropriate; the second column specifies $\vec{k}$ (see text); the third column gives the number of like vectors; the rth through seventh columns gives the energy eigenvalues. Energy is given in electron volts, and the zero of energy taken to be the bottom of the first band.

Energy band structure of aluminum

BSW	k	Like k	Band 1	Band 2	Band 3	Band 4
Γ	000	1	0.000	26.880	28.398	36.883
Δ	100	6	0.141	24.722	26.235	32.431
Δ	200	6	0.570	22.851	24.353	28.273
Δ	300	6	1.284	21.269	22.726	24.438
Δ	400	6	2.285	19.974	20.625	21.654
Δ	500	6	3.568	17.428	18.966	20.545
Δ	600	6	5.130	14.445	18.247	19.809
Δ	700	6	6.940	11.777	17.815	19.372
X	800	3	8.463	9.967	17.672	19.226
Σ	110	12	0.285	22.563	24.083	32.569
	210	24	0.713	20.693	22.207	28.405
	310	24	1.428	19.110	20.613	24.537
	410	24	2.428	17.815	19.273	20.992
	510	24	3.711	16.808	17.465	18.494
	610	24	5.272	14.569	16.089	17.671
	710	24	7.082	11.912	15.657	17.224
z	810	12	8.607	10.102	15.513	17.077
Σ	220	12	1.144	18.823	20.343	28.831
	320	24	1.858	17.240	18.755	24.957
	420	24	2.858	15.945	17.449	21.378
	520	24	4.142	14.938	16.396	18.126
	620	24	5.702	14.219	14.888	15.916
	720	24	7.511	12.321	13.787	15.378
z	820	12	9.039	10.517	13.643	15.223
Σ	330	12	2.577	15.657	17.179	25.670
	430	24	3.576	14.362	15.880	22.086
	530	24	4.859	13.355	14.861	18.800
	630	24	6.418	12.636	14.095	15.848
	730	24	8.226	12.204	12.903	13.933
z	830	12	9.758	11.189	12.060	13.688
Σ	440	12	4.581	13.068	14.592	23.087
	540	24	5.863	12.060	13.582	19.795
	640	24	7.420	11.341	12.853	16.808
	740	24	9.223	10.909	12.374	14.190
w	840	6	10.765	10.765	11.808	12.782
Σ	550	12	7.152	11.053	12.586	21.084
	650	24	8.702	10.334	11.872	18.090
	750	8	9.902	10.457	11.478	15.434
k	660	4	9.614	10.208	11.235	19.666
Λ	111	8	0.429	21.044	25.689	32.714
	211	24	0.857	19.173	24.012	28.552
	311	24	1.571	17.589	22.411	24.691
	411	24	2.571	16.292	20.817	21.404
	511	24	3.855	15.276	17.711	20.183
	611	24	5.416	14.426	14.889	19.417
	711	24	7.225	12.045	14.169	19.011

Energy band structure of aluminum

BSW	k	Like k	Band 1	Band 2	Band 3	Band 4
s	811	12	8.751	10.241	14.018	18.866
	221	24	1.288	17.304	22.148	28.976
	321	48	2.002	15.721	20.560	25.103
	421	48	3.002	14.425	19.246	21.533
	521	48	4.285	13.415	17.942	18.535
	621	48	5.845	12.687	15.171	17.596
	721	48	7.654	12.131	12.640	17.149
	821	24	9.183	10.633	12.180	17.002
	331	24	2.720	14.140	18.984	25.815
	431	48	3.720	12.845	17.683	22.232
	531	48	5.002	11.837	16.657	18.955
	631	48	6.561	11.116	15.646	16.251
	731	48	8.365	10.678	13.213	15.590
	831	16	9.902	10.457	11.478	15.434
	441	24	4.725	11.552	16.395	23.232
	541	48	6.005	10.546	15.383	19.941
	641	48	7.558	9.832	14.645	16.963
q	741	24	9.214	9.548	13.935	14.574
	551	24	7.289	9.548	14.385	21.229
	651	24	8.651	9.024	13.662	18.236
Λ	222	8	1.719	15.495	24.817	29.412
	322	24	2.433	13.912	23.218	25.548
	422	24	3.433	12.617	21.668	22.215
	522	24	4.715	11.609	18.598	20.932
	622	24	6.274	10.888	15.616	20.247
	722	24	8.079	10.448	12.961	19.811
u	822	8	9.614	10.208	11.235	19.666
	332	24	3.151	12.332	21.652	26.251
	432	48	4.150	11.037	20.341	22.677
	532	48	5.431	10.032	19.080	19.634
	632	48	6.984	9.319	16.315	18.682
	732	24	8.651	9.024	13.662	18.236
	442	24	5.153	9.747	19.063	23.668
	542	48	6.428	8.748	18.040	20.387
q	642	24	7.804	8.211	17.071	17.638
	552	12	7.521	7.942	17.050	21.664
Λ	333	8	3.869	10.772	24.638	26.984
	433	24	4.866	9.480	23.102	23.636
	330	24	2.577	15.657	17.179	25.670
	633	12	7.521	7.942	17.050	21.664
	443	24	5.862	8.196	22.048	24.401
q	543	24	6.951	7.381	20.802	21.343
l	411	4	6.668	7.114	25.114	25.641

ces. We present here in tabular form (Table IV) somewhat more complete matrix in the Brillouin one which should be of value in checking the lequacy of computer programs for generating ind structure. To avoid fractions, the wave vectors $\vec{k}$ are given here in units of $\pi/4a$, where a is e lattice constant. These are presented in Ashroft's[10] choice of $\frac{1}{48}$ symmetry sector. Burdick's[41] scussion details the method of constructing this esh of 89 $\vec{k}$ values. Since the entire Brillouin one is not directly sampled in this type of calcuation, one can infer the contributions from the ntire zone to a calculated property via the number f vectors equivalent by symmetry to those direct- used; the algorithm for generating the number f "like vectors" is given by Brust.[33]

We also present in Fig. 10, conventional graphal representation of energy bands for various ymmetry axes and zone surfaces. The bands are presented along more lines, in our results, than elsewhere.[10]

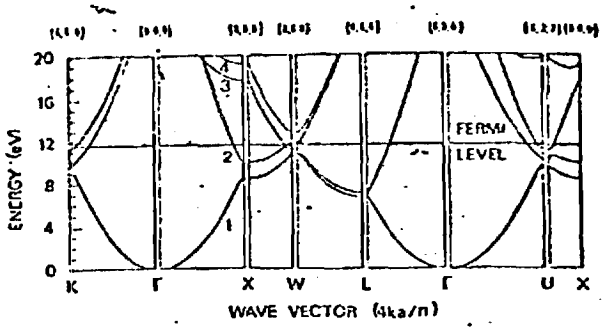


FIG. 10. Energy band structure of Al based on a four-OPW (orthogonalized-plane-wave) model. The results are given within the irreducible sector of the Brillouin zone. Ashcroft's pseudopotential was employed. Bands are indexed 1–4, at fixed wave vector, in order of increasing energy.

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Appendix III

(Submitted to Phys. Rev. B March 1976)

Luminescence Induced by Ion Impact on Alkali Halide Crystals at High Temperatures (-160°C to 200°C)*

A. I. Bazhin,† E. O. Rausch and E. W. Thomas

School of Physics

Georgia Institute of Technology, Atlanta, GA 30332

A study has been made of luminescence induced by 25 keV H^+ and He^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependance of luminescence, and the effect of bleaching, in KCl and KBr. The peak intensity in the luminescent spectrum is independent of temperature from -160°C to -70°C, rises to a maximum at about -10°C then falls monotonically for further increase in temperature. The dependance of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole-centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to O_2 we also observe an additional band characteristic of O_2^-.

I Introduction

The interaction of ionizing radiation with the solid state causes electron excitations in the form of electron-hole pairs or excitons; these subsequently decay either by a non-radiative transition with the formation of phonons and lattice defects, or by radiative transitions leading to luminescence. Intrinsic luminescence of alkali halides has been extensively investigated (see for example the pioneering work in references 1,2,3, and 4); this is a fundamental luminescence associated with recombination of excited electrons with self trapped hole (V_k centers). Intrinsic luminescence is observed for temperatures where the V_k center is stable, and for most alkali halides the radiative efficiencies and lifetimes of V_k centers begin to fall off strongly at temperatures above 100°K due to non radiative recombination.[4] Although efficiency of intrinsic luminescence is relatively low at temperatures of 150°K and above, Ikeya and Crawford[5] observed a new band of luminescence in NaCl at 310 nm., which is not quenched at temperatures of 150°K and above. They suggest that this band is associated with electron recombinations with the V_k center at some unknown impurity or by electron recombination at some type of V center formed by irradiation at room temperature. Luminescence induced by electron impact on alkali halides at 90 to 300°K temperatures was extensively studied by Pinard and co-workers.[6,7] They proposed a mechanism where F centers are responsible for luminescence and quenching is related to V_3 and V_4 centers. In a study of X-ray induced luminescence at high temperatures in NaCl,

Spicer[8] suggests that the luminescence centers are of the V_2 and V_4 type and emission occurs as electrons fall into these centers. Other published studies of luminescence in alkali halides at high temperatures include work on thermoluminescence,[9,10,11] aquoluminescence,[12,13] neutron induced luminescence[14] and X-ray induced luminescence in string crystals.[15,16] Previous work on luminescence induced by energetic ion impact on high temperature crystals is restricted to the work of Alekseev et al.[17] concerning bombardment of KCl and NaCl by H^+; here the emission was associated with water molecules in the excited triplet state, present in the crystals as uncontrolled impurities.

In the present paper we investigate luminescence of certain alkali halides induced by the impact of H^+ and He^+ ions with energies of 5 to 25 keV. Targets of principal interest in this work were NaCl, NaF, KCl and KBr; various target temperatures in the range -160 to 200°C were employed. The high density of electron excitation close to the target surface causes a high efficiency for defect generation in the cation sublattice and the formation of hole centers that are stable at room temperature.

II Experimental Procedure

The apparatus used for this work is essentially the same as that previously described for studies of light emission when ions strike metal surfaces;[18] we shall therefore give only a very brief description here. The ions are formed in an rf discharge source, accelerated and mass analyzed before being collimated and directed onto the target. Light emission from the point of beam impact on the target was viewed by a conventional scanning monochromator observing through a sapphire window. The monochromator axis was perpendicular to the direction of the incident beam; the angle between the beam and the target surface normal could be varied but was kept at 45° for the experiments described here. The detection sensitivity of the optical system had been previously calibrated utilizing a standard tungsten filament lamp of known emissive power. The target samples were single crystals of alkali halides supplied by the Naval Research Laboratory (Washington, D.C.); they had been zone refined and had a nominal total impurity level of a few p.p.m. or less. The samples were cleaved to a size of approximately 10 x 6 x 1 mm immediately before introduction into the vacuum system. The target was mounted on a standard manipulator by Varian, providing three axes of translational motion and one axis of rotation. A specially designed target holder was employed that had a filament for heating the target region and tubes to conduct liquid nitrogen and thereby provide cooling. A number of thermocouples were provided to measure the temperature on the bombarded face of the crystal.

The target chamber provided a vacuum environment with a base pressure of around 10^{-9} torr for the work described here. After introduction into the vacuum system the targets were annealed at a temperature of 400°C for at least one hour in an attempt to remove surface contamination and to anneal defects in the crystal. The area of the target irradiated by the ion beam was approximately 5 mm^2 and the beam current density was generally about 10 uA/cm^2; at these current densities there was no evidence of target surface charging or electrical breakdown on the surface. Tests showed that reducing the ion beam current density by two orders of magnitude did not change the shape of the observed spectra; moreover the intensity of the spectrum was linearly proportional to beam current throughout this range. We would note that the average depth of penetration of a 25 keV H^+ ion in KCl is about 400 nm; for a 25 keV He^+ ion the depth is about 150 nm.[19] Thus the region of excitation is very close to the surface, in contrast to studies of luminescence under X-ray, and U-V photon excitation where much greater penetration depths are involved.

This work was primarily concerned with the impact of H^+ and He^+ ions on alkali halides; the observed spectra were the broad bands of luminescence that we shall discuss shortly, with some line emission in the Sodium-D when crystals containing Na were employed; this sodium emission is from sputtered atoms in excited states. Some preliminary experiments were performed with neutral hydrogen beams which gave precisely the same spectra as for H^+ and He^+ impact. We also used Ar^+ beams and observed again the same basic luminescence spectrum but with stongly enhanced emissions from sputtered alkali atoms. Spectra induced by H^+ and He^+ impact were essentially

the same for new crystals and for crystals that had suffered a preliminary bombardment with Ar^+; since the argon beam will readily sputter the surface this observation suggests that surface contamination did not strongly contribute to the observed emission spectra. Some preliminary experiments were also performed using crystals supplied by the Harshaw Chemical company and stated to be of optical purity; the observed spectra were not significantly different from those observed with the higher purity crystals supplied by the Naval Research Laboratory. Crystals from the latter source were employed for all the detailed measurements presented here.

Various types of data are presented here. We have recordings of the ion-induced luminescence spectra to display the relevant spectral features. We show how certain of the features vary with the temperature of the target and with the dose to which the target has been subjected. In studies of the dose dependence we measure the intensity as a function of time under continuous bombardment by a beam of constant current density. We have no knowledge of the particle density distribution in the ion beam; if inhomogeneities were present then the local dose rate might differ significantly from the dose rate integrated over the ion beam's cross sectional area. Consequently we consider it more accurate to present data as a function of the measured parameter, time, rather than the derived parameter of dose.

III Results and Discussion

In figs. 1 and 2 are shown spectra induced by ion beam impact on targets of KCl, KBr, NaCl and NaF; the reader is referred to the captions for the precise conditions of bombardment in each case. The spectra are corrected for the variation of relative sensitivity with wavelength but have not been placed on an absolute scale. The spectra are typical for these samples and remain essentially unchanged in basic shape if one alters beam energy or interchanges protons and He^+ ions; such changes however, do alter the intensity of the emission. The spectra are wide luminescent bands varying in shape between the various crystals; in addition for the NaCl crystal we observe a narrow emission line at the NaD wavelength corresponding to atomic line emission from sputtered sodium atoms. In our following discussions we shall concetrate principally on the KCl and KBr spectra and consider in detail the effects of annealing, temperature variation, and dose.

An initial test was made to determine whether any of the band spectrum was linked to impurities. We recorded the ion-induced luminescence spectrum from KCl and KBr crystals both in their freshly cleaved state before annealing and also after annealing for 5 hours at 450°C in the 10^{-9} torr vacuum environment. We found that annealing caused a substantial reduction of intensity at wavelengths around 530 nm, suggesting a band at this point associated with impurities. To confirm this we exposed annealed samples to nitrogen and oxygen gas for five minutes or more at a pressure of 10^{-6} torr. Nitrogen caused no change to the spectrum but oxygen caused

a rise of intensity at 530 nm by a factor of three and restored the spectrum to the form observed before annealing. Fig. 3 shows a spectrum of KBr after oxygen absorption which should be compared with the typical spectrum of an annealed sample shown as Fig. 1C. The annealed sample shows a small residual peak at 530 nm but the sample with oxygen exposure is dominated by the 530 nm peak which covers and obscures the peak at 480 nm. Similar results are found with KCl and NaCl samples. We believe that the 530 nm band is due to oxygen impurities on the surface. Rolfe et al.[20] have studied the fluorescence of NaCl, KCl, KBr doped with O_2^- and find a band which peaks at 530 to 550 nm, depending on the crystal; we do not, however, observe the vibrational structure seen when O_2^- is a substitutional impurity.[20] In the work that follows all crystals were first annealed to a temperature of 400°C for an hour or more to reduce or remove the influence of the oxygen contamination.

The most significant features of the room temperature spectra of KCl and KBr are peaks at 480 nm and 500 nm respectively; we shall later show that these are due to recombination of electrons from the conduction band with V_3 centers. At low temperatures (Fig. 2) we also observe for these same targets a weak peak at lower wavelengths, 370 nm for KCl and 350 for KBr; we shall later show that these peaks are due to recombination of conduction band electrons with V_4 centers. The low wavelength peaks are strongly overlapped by the more intense high wavelength peak and show up on the spectra as only weak shoulders; they are, however quite reproducible.

In fig. 4 we show measurements of luminescent intensity as a function

of temperature for KCl and KBr crystals. The intensity is measured at 480 nm for KCl and 500 nm for KBr with a spectral resolution of 4.8 nm; these wavelengths correspond to the peaks of intensity in these spectra. It was found that the ion beam impacting on a crystal at low temperatures could cause a significant temperature rise. Consequently the ion beam was pulsed on for only two seconds at each temperature in order that temperature rise should be kept less than 1°C. Fig. 4 shows that luminescent intensity is constant as temperature rises from -150°C to about -50°C then rises to a weak maximum at about -10°C and decreases for further increase in temperature. Provided the crystal had been properly annealed before commencing the measurement we found no difference between data taken as temperature increased and data taken with decreasing temperatures.

If the luminescence centers are lattice defects arising during ion bombardment then a study of intensity as a function of dose should represent the formation of the relevant radiation defects. To study such behaviour an annealed crystal was bombarded continuously for a period of 10 to 20 minutes using a H^+ beam of 10 $\mu A/cm^2$ flux density. A continuous record of intensity as a function of time, and therefore dose, was performed. Figs. 5 and 6 show the results for KBr and KCl crystals at room temperature and at a lower temperature. Low temperature behaviour (Fig. 5) shows three distinct regions. First a rapid decrease of intensity over a period of one minute; secondly a rising intensity extending over a bombardment time of 3 to 8 minutes, depending on the sample; finally the third region is a very slow decline of intensity which appears to continue indefinitely. By contrast the room temperature behaviour (Fig. 6) is an initial rapid rise, followed by a rapid fall and finally at bombardment time of 8 minutes or more a slow decline that continues indefinitely.

In the studies of dose dependence (Figs. 5 and 6) there are regions where intensity increases as a function of dose; these suggest that the centers responsible for luminescence are created by ion bombardment. However, the intensity of luminescence is not zero at the commencement of bombardment so that some luminescent centers are already present in the unbombarded crystal despite the preliminary annealing procedure. The fact that intensity is a function of temperature shows that the formation, and the stability, of the defects responsible for luminescence is temperature dependant. It is known that during irradiation of KBr and KCl at temperatures close to room temperature one forms[21] stable electron centers of the F and F_2(M) types and also hole defects of the V_3 type (this center being designated V_x by Lushchik et al.[16]). In order to try to separate the roles of these different centers we performed some simple light bleaching experiments. First the crystals were bombarded with H^+ ions for a time of ten minutes or more so that the luminescence intensity corresponded to a point on Fig. 6 in the final section of the dose dependance where intensity decreases slowly as dose is increased. Then, with the ion beam removed, the crystal was exposed to light in the F band absorption region provided by a tungsten filament lamp and suitable absorption filters; we used 560 nm for KCl and 620 nm for KBr with a band width of 140 nm in both cases. The bleaching was terminated after 30 minutes and ion bombardment recommenced. The intensity of the ion-induced luminescence was unchanged by the attempt at F center bleaching. We also exposed the crystal to unfiltered white light which should bleach more complicated electron centers; again no effect was observed. Thus no effect of bleaching

was found and we conclude that the centers of luminescence can be V_3-centers which are known[21] not to be bleached by white light.

We propose that the V_3 center is responsible for the principal luminescent intensity at 480 nm in KCl (Fig. 1C and 2C) and 500 nm in KBr (Fig. 2A and 2B); it is known[21,22] that the V_3 center is stable up to 200°C. At low temperatures we also observe a small peak at 370 nm in KCl and 350 nm in KBr (see Fig. 2B and 2C); we propose that the V_4 center is responsible for this feature. The low wavelength peak does not appear to be connected with impurities and as temperature is raised the feature is no longer apparent. It is known that at temperatures below -30°C the V_4 center occurs in addition to the V_3 center. However, at all temperatures considered here the luminescence we identify as due to V_3 centers, predominates. In Fig. 7 are shown the structures postulated for the V_3 and V_4 centers.[16,22] The X_3^- molecule occupies a divacancy to form a V_4 centers, and the X_3^- molecule occupies one cation and two anion vacancies to form the V_3 center. If, as we suggest, the V_3 and V_4 centers are responsible for these emission bands then the sum of energy of emitted photon and the energy of V_3 and V_4 center photon absorption, should equal the band-to-band energy. In Fig. 7 we show an energy level scheme appropriate to KCl with the suggested radiative recombination transition. In table I we list the band gap energies for KCl, KBr and NaCl with the energy of photon emission which we identify as due to recombination of electrons with the V_3 and V_4 centers; also listed are the photon energies of maximum absorption ascribed by others[26,28] as due to the V_3 and V_4 centers. In KCl the band gap is quoted[24] as 8.5 eV

and the energies for photo absorption by V_3 and V_4 centers are 5.85 eV and 5.16 eV respectively;[26,28] thus the predicted energies of photon emission in recombination of electrons with V_3 and V_4 centers are 2.65 and 3.34 eV respectively. Hence we expect emission at 468 nm for the V_3 center and 371 nm for the V_4 center; quite close to our observed peaks at 480 nm and 370 nm. This reinforces our conclusion that the observed luminescene is due predominatly to recombination of electrons with V_3 centers and that at low temperatures there is an additional small feature caused by recombination of electrons with V_4 centers.

It is difficult to make precise statements about the width of our observed luminescence bands since there is considerable overlap between the prominent V_3 band, the weak V_4 band and residual effects of the O_2^- impurity band. However, a rough estimate of the V_3 band width at half maximum for KCl (Fig. 2A) is 1.1 eV; this is consistent with the width of the V_3 absorption band which is about 1.2 eV in the measurements of Seretlo.[21]

With the identification of the emission as being due to electron recombination with V_3 and V_4 centers we should now be in a position to understand the dependance of intensity on temperature and irradiation dose. The intensity of the ion-induced luminescense will undoubtedly depend on the rate of electron excitation to the conduction band and on non-radiative decays of such electrons; also intensity will depend on the density of relevant recombination centers through their rates of creation and rates of annealing. Thus the relationship of luminescent intensity to dose and

temperature is more complex than the relationship of directly measured V_3 and V_4 center density to these same experimental parameters. It would be presumptuous, and possibly misleading, to attempt a modeling of the phenomenon based only on the measured parameter of intensity; supporting information on the directly measured defect-center concentrations would be necessary in order to develop a reliable quantitative understanding. Nevertheless a general qualitative explanation may be achieved by studying the close correlations between the present work and previously published direct measurement of F, V_3 and V_4 center densities induced by x-ray, electron and ion irradiation. We should note that V_3 and V_4 type centers are complementary to the F center and should therefore exhibit the same rate of formation with dose. The ion fluxes used in these studies ($10\mu A/cm^2$) represent a rather high dose rate compared with previous studies of defect center concentration induced by X-ray irradiation. In the work of Alekseev[17] on bombardment of NaCl by 30 keV H^+ it was found that the F center concentration saturated at 5.35×10^{18} cm^{-3}. By comparison the studies of F center formation under X-ray irradiation by Seretlo[21] involved a maximum F center density of 1.5×10^{17} cm^{-3} in the irradiated sample; most irradiations were smaller.

Hughes and Pooley[29] have studied F center growth in KCl under bombardment by protons of 100 keV energy and above at high doses. F center concentration increases to a saturation and then decreases with further increase of dose. This behavior is explained in terms of a spontaneous recombination (athermal annealing) of intersticials and vacancies. Two competing machanisms are involved.[29] In the first, one argues that an intersticial (or vacancy) formed within some critical distance of a vacancy (or intersticial) will recombine so that no new defect center is produced. The second mechanism is a "back reaction" where F centers diffuse and either recombine with intersticials they encounter or else form F center agregates. These mechanisms together can predict a rise in F center (and hence V_3 and V_4 center) concentration, followed by saturation, and a subsequent decrease. We observe such behavior for luminescence in room temperature irradiation (Fig. 6) and for most of the low temperature irradiation (Fig. 5); thus emission intensity mirrors the expected behavior of V_3 and V_4 center density. We note that Hughes and Pooley[29] find F center concentration to staurate at a dose of about 10^{19} ions/m^2 for 100 keV impact at room temperature. In comparison, our data for 25 keV H^+ impact shows saturation at a dose of about 4×10^{19} ions/m^2 at room temperature and 2×10^{20} ions/m^2 at -150°C; thus our doses for saturation of luminescence are quite comparable with the previously observed[29] dose for saturation of F center concentration. We can provide no explanation of the low dose behavior in Fig. 5 where an initial rapid decrease of intensity is observed. However we note that similar behavior is seen in cathodoluminescence studies by Nouailhat et al.,[7] and in conductivity studies of string crystals by Melik-Gaikazyan et al.[15] This behavior has been ascribed[15] to the destruction of pre-irradiation defects.

Neglecting the effects of non-radiative electron transitions, the luminescence intensity as a function of temperature (Fig. 4) should mirror the V_3 center concentration. Seretlo [21] has studied thermal annealing of V_3 centers that were created by x-ray irradiation. For the highest irradiation densities utilized, Seretlo observes the V_3 center concentration to decrease generally monotonically with temperature above 30°C, with the exception of a small, unexplained, peak at 70°C. Our data on luminescence intensity of the V_3 band as a function of temperature above 0°C shows essentially the same behavior, apart from the unexplained peak. At temperatures below -20°C our intensity in the V_3 band decreases and becomes constant. In this temperature region we observe increasing prominence of the low wavelength emission band ascribed to recombination on V_4 centers; the V_4 center is of course an alternative final state for displaced atoms. We conjecture that the sum of V_3 and V_4 center concentrations may remain relatively constant at low temperatures but that the V_4 centers assume greater importance than at room temperatures and the V_3 center luminescence therefore decreases.

IV Conclusion

The luminescence induced by impact of 25 keV H^+ and He^+ ions on KCl and KBr consists of an intense broad band peaking at around 500 nm. We identify this band as due to electron recombination with V_3 centers. At low temperatures there is a second weak feature around 360 nm which we identify as due to electron recombination with V_4 centers. The photon energies at the emission intensity peak are consistent with the known band gap and known energies of the V_3 and V_4 centers established by photoabsorption measurements. The behavior of the luminescence intensity as a function of temperature and dose is quite consistent with other more direct measurements of F, V_3, and V_4 center formation.

V Acknowledgement

We are indepted to Dr. Howard Lessof of the Naval Research Laboratory, Washington, D.C. for the supply of many of the samples used in this work. Also we acknowledge the assistance of Dr. M. Zivitz in the early states of this work. One of us (A.I.B.) acknowledges support from the International Research and Exchanges Board.

*Supported in part by a grant from the Division of Materials Research of the National Science Foundation.

+Visiting Soviet Scientist under the "U.S.A./U.S.S.R. Young Faculty Exchange Program." Permanent address, Department of Physics, University of Donetsk, Donetsk, USSR.

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Table I

Table of known band gap energies and known photon energies for absorption maxima in the V_3 and V_4 bands presented with the photon energies. (and wavelengths) of the peak intensity observed in the present luminescence studies. Band I is the high wavelength band we ascribe to the V_3 center and Band I is the low wavelength band we ascribe to the V_4 center.

Sample	Energy Gap(eV)	Absorption Band Maxima (eV)		Observed Luminescent Band Maxima			
				Band I		Band II	
		V_3	V_4	Energy (eV)	Wavelength (nm)	Energy (eV)	Wavelength (nm)
NaCl	8.6[a]	5.9[b]	5.56[c]	2.76	450	3.31	375
KBr	7.8[a]	5.35[c]	4.5[d]	2.48	500	3.54	350
KCl	8.5[a]	5.85[c]	5.16[e]	2.58	480	3.35	370

References

a. Ref. 24
b. Ref. 25
c. Ref. 26
d. Ref. 27
e. Ref. 28

Figure Captions

1. Luminescence spectra of certain alkali halides at room temperature under bombardment by 25 keV projectiles. A, NaCl bombarded by a $10\mu A/cm^2$ H^+ beam at a temperature of 20°C; B, NaF bombardment by a $6\mu A/cm^2$ He^+ beam at a temperature of 22°C; C, KBr bombarded at a $10\mu A/cm^2 H^+$ beam at a temperature of 22°C.

2. Luminescence spectra of KCl and KBr at low temperature under bombardment by a $10\mu A/cm^2$ beam of 25 keV H^+ ions. A, KCl at -29°C; B, KCl at -50°C; C, KBr at -150°C.

3. Luminescence spectrum of KBr after absorption of O_2 at 10^{-6} torr; projectile beam is 25 keV He^+ at a current density of 6 $\mu A/cm^2$ and target temperature is 29°C.

4. Dependence of the luminescence intensity on target temperature. Targets are KCl and KBr; bombarding beam is 25 keV H^+ at a density of 10 $\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

5. Dependence of luminescence intensity on dose for targets at low temperature. Targets are KCl at -135°C and KBr at -150°C; bombarding beam is 25 keV H^+ at a density of $10\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

6. Dependence of luminescence intensity on dose for targets at room temperature (22°C). Targets are KCl and KBr; bombarding beam is 25 keV H^+ at a density of 10 $\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

7. Diagram of the structure ascribed to V_3 and V_4 centers with an energy level diagram for KCl showing the position of the energy levels associated with such centers.

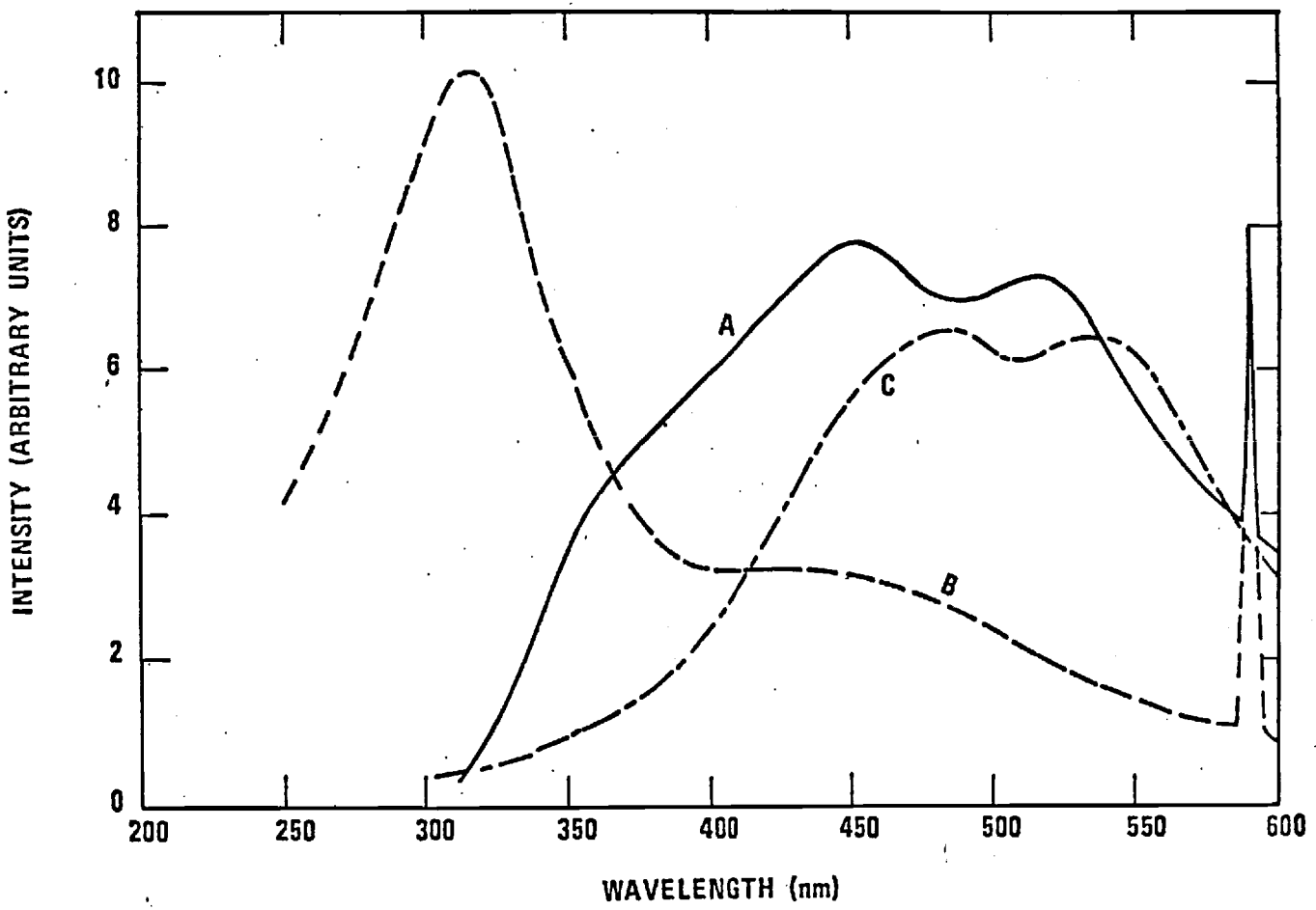

INTENSITY (ARBITRARY UNITS)
0
2
4
6
8
10
200
250
300
350
400
450
500
550
600
WAVELENGTH (nm)
A
B
C

Fig. 1

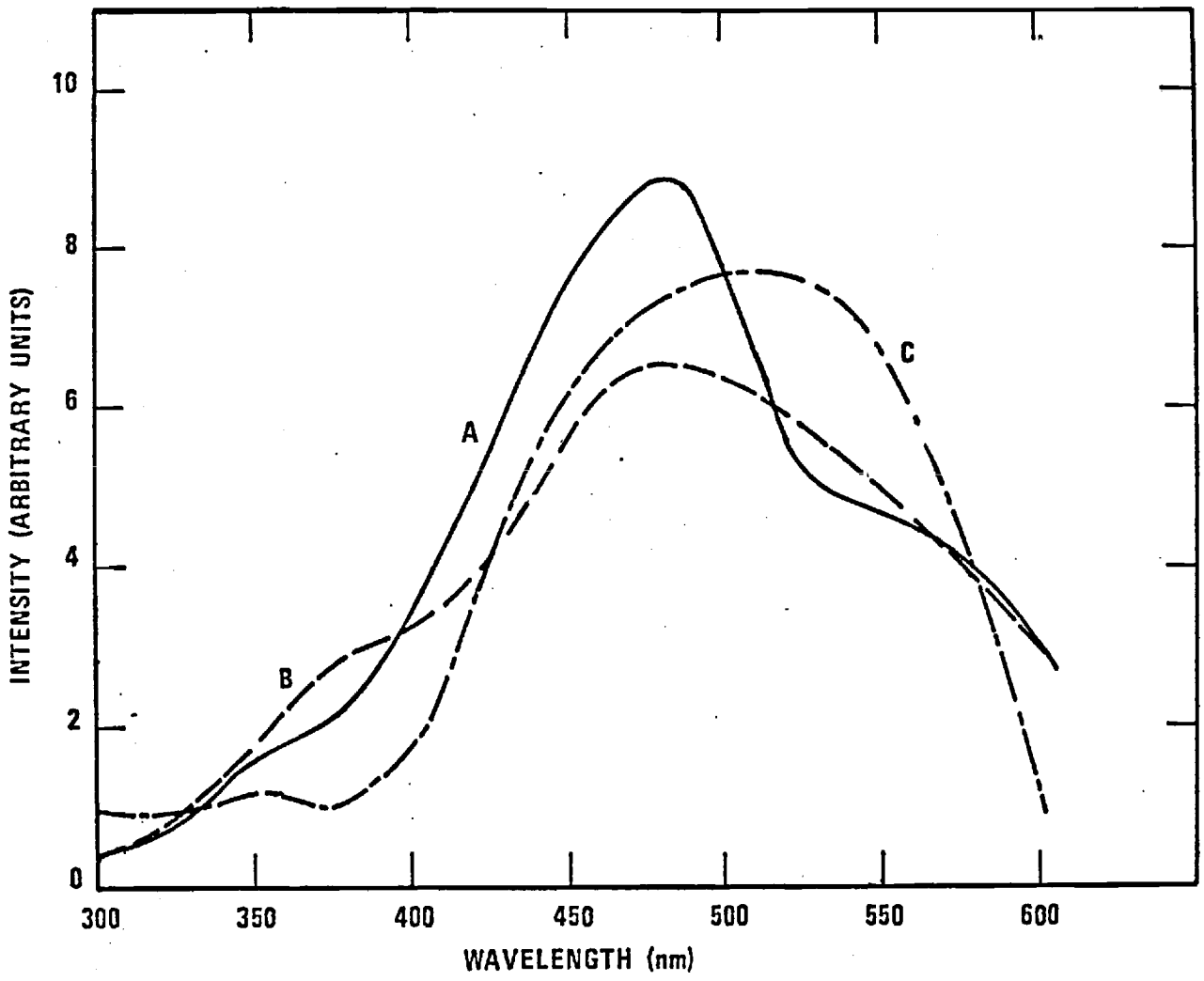

INTENSITY (ARBITRARY UNITS)
10
8
6
4
2
0
300
350
400
450
500
550
600
WAVELENGTH (nm)
A
B
C

Fig 2

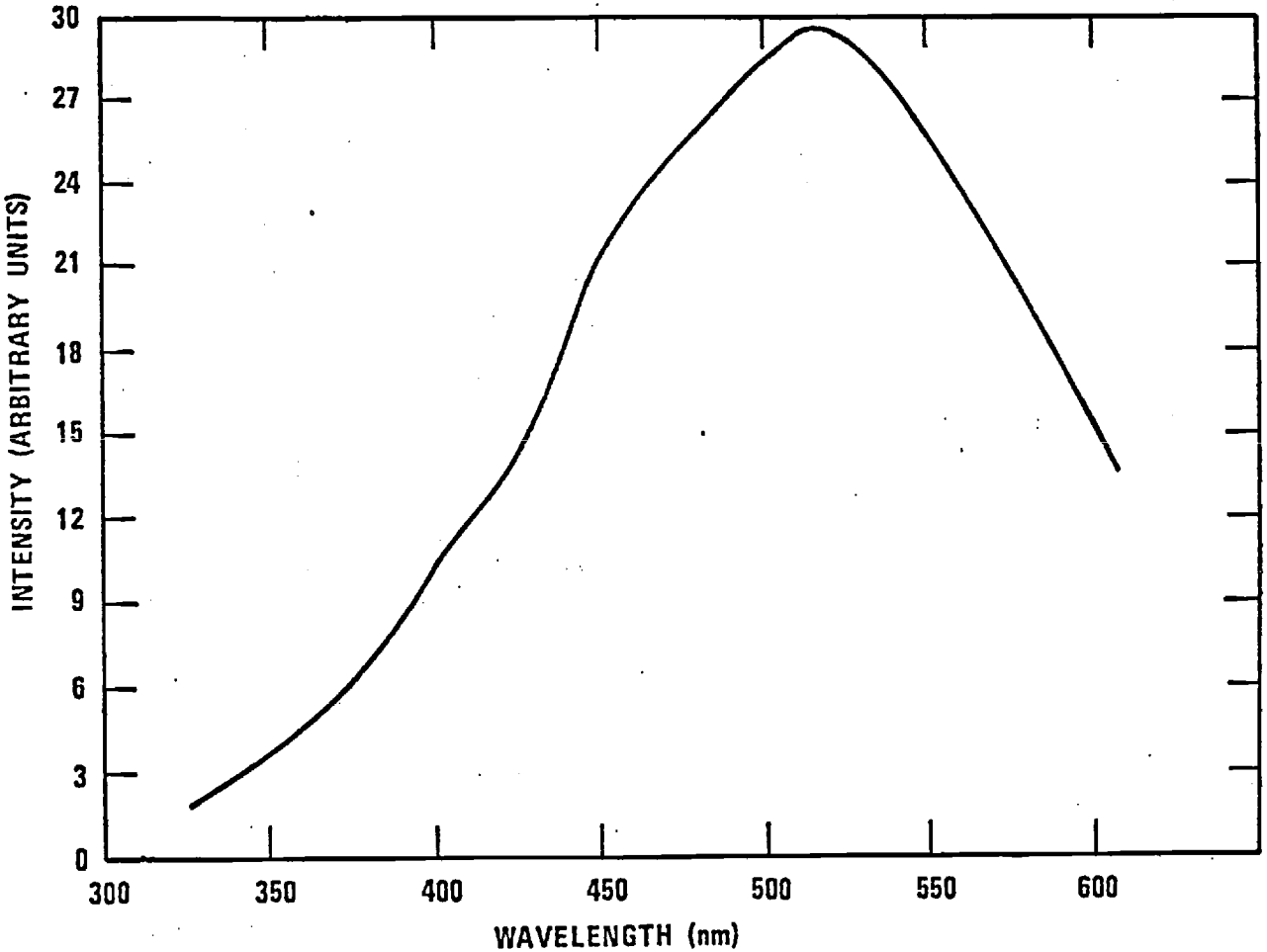

INTENSITY (ARBITRARY UNITS)
30
27
24
21
18
15
12
9
6
3
0
300
350
400
450
500
550
600
WAVELENGTH (nm)

Fig 3

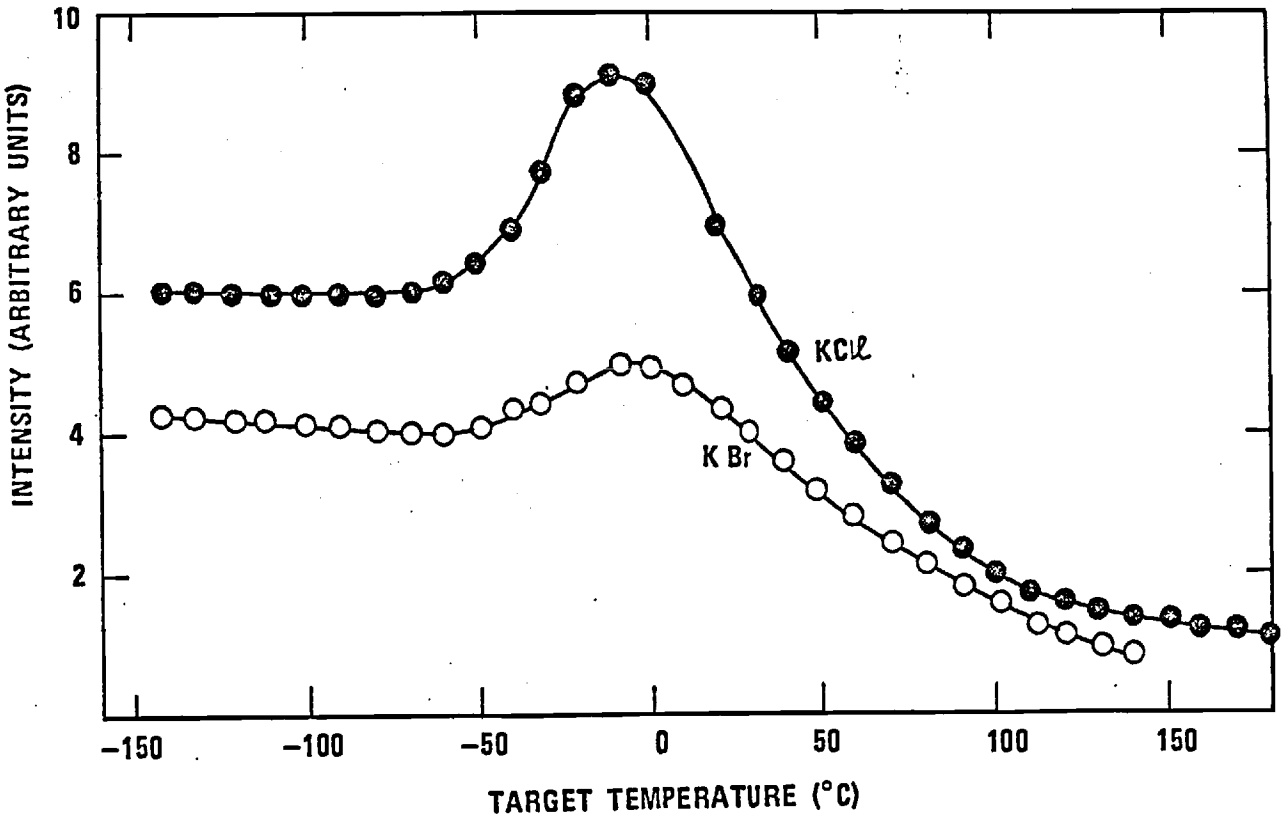

INTENSITY (ARBITRARY UNITS)
10
8
6
4
2
KCl
K Br
−150
−100
−50
0
50
100
150
TARGET TEMPERATURE (°C)

Fig. 4

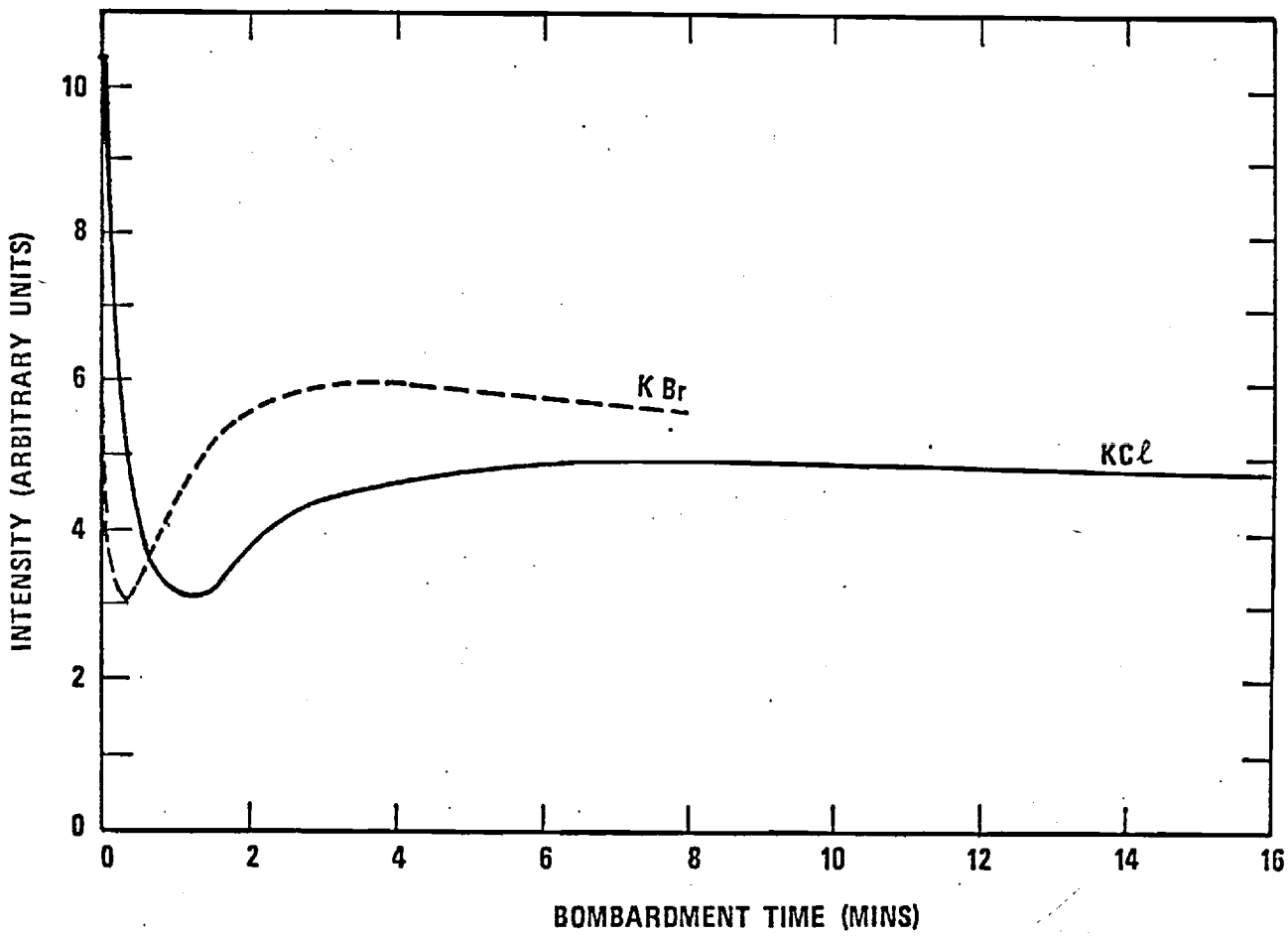
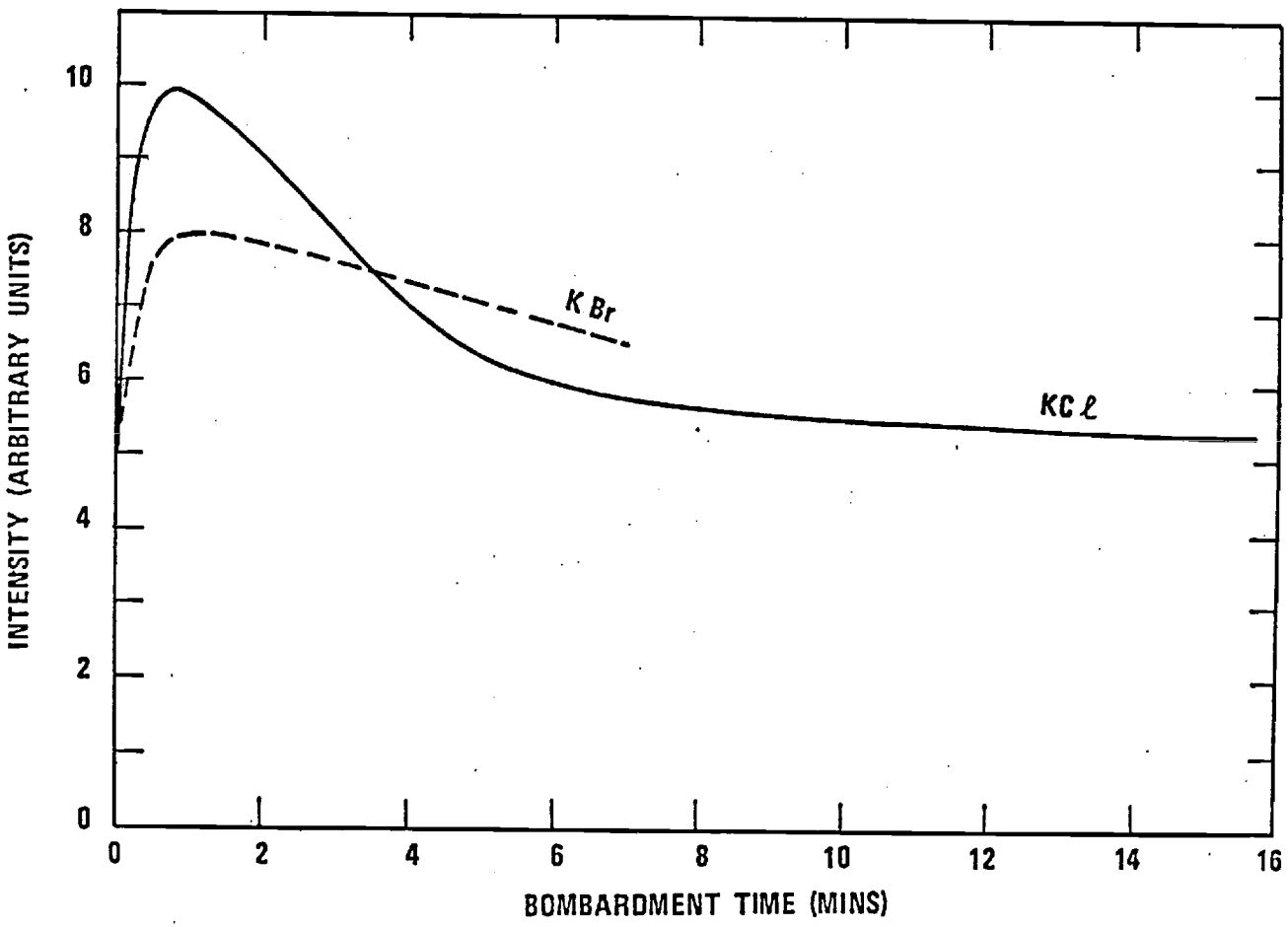

INTENSITY (ARBITRARY UNITS)
0
2
4
6
8
10
0
2
4
6
8
10
12
14
16
BOMBARDMENT TIME (MINS)
K Br
KCℓ

Fig 5


INTENSITY (ARBITRARY UNITS)
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8
6
4
2
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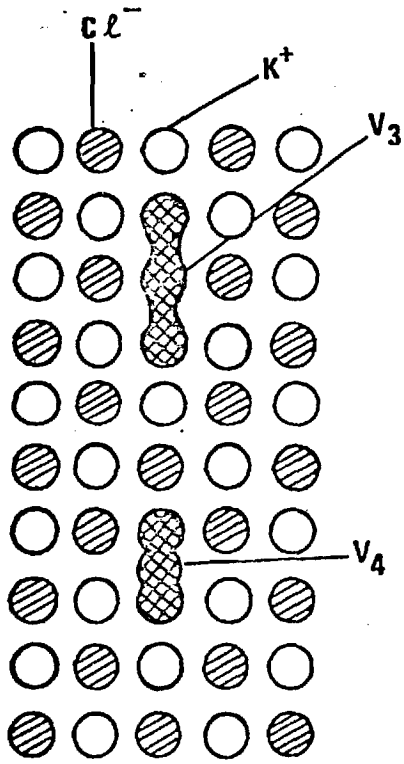
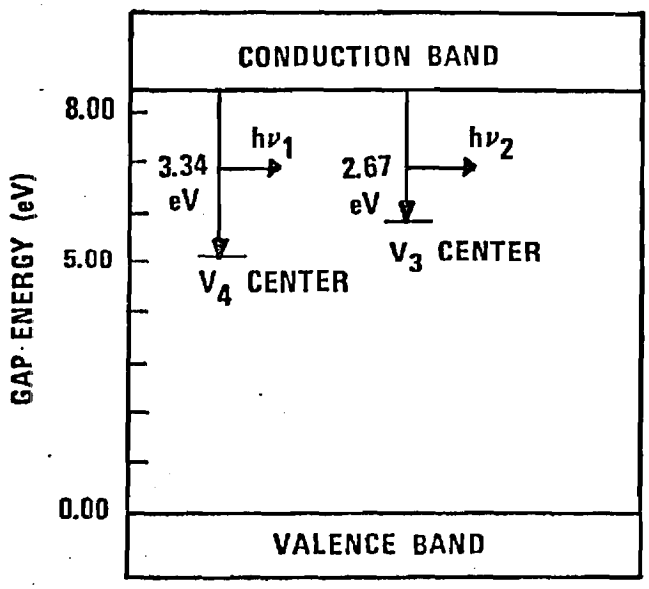
2
4
6
8
10
12
14
16
BOMBARDMENT TIME (MINS)
K Br
KC ℓ

Fig 6


Cl⁻
K⁺
V3
V4

a


CONDUCTION BAND
8.00
5.00
0.00
GAP ENERGY (eV)
3.34 eV
hν1
2.67 eV
hν2
V4 CENTER
V3 CENTER
VALENCE BAND

b

Fig 7

G-411-630

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(404) 894-5201

SCHOOL OF PHYSICS

February 8, 1977

Dr. Dean L. Mitchell
Solid State Physics Program
Division of Materials Research
National Science Foundation
1800 G Street
Washington, D.C. 20550

Dear Dr. Mitchell:

This letter is to serve as the annual technical report on our grant DMR73-02317 A02.

The original proposal for the current twelve month period called for a study of optical light emission induced by energetic heavy ion impact on solids. The program was supposed to have two facets; one was a study with alkali halide crystals and the other with metal targets. At the time of our last renewal you communicated to me (by telephone) some adverse comments by your referees, concerning the proposed work with alkali halides and other insulators. I fully concurred with your opinion that our work with metals was the more interesting facet of our proposed program, and that an attempt should be made to develop this area into a study of surface chemistry. With these scientific comments in mind (and in view of the fact that the support granted was somewhat less than requested) I determined that we should de-emphasize that part of the program associated with intrinsic luminesce in insulators and concentrate on radiation emitted from metals and from chemical reactions on the surface of alkali halides. Accordingly the present report includes a discussion of a chemical reaction leading to formation of CN radicals on alkali halides and of continuum luminescence from metals; our limited work on luminescence of alkali halides is discussed only briefly. The discussions given here are only summarys and I would refer you to the accompanying reprints for full details.

A. Studies with Metal Targets

One of the original objectives of this program was to identify the source of continuum light emission observed when certain transition metals are bombarded with heavy ions (e.g. 5 to 30 keV Ar^+). This emission had been observed by many groups but its origin was a mystery. An important characteristic was that the source of emission extended up to one centimeter in front of the bombarded target, indicating that the emitters were ejected from the target. We have shown quite unambiguously that the phenomenon occurs only when the surface is contaminated and that the spectra recorded by other groups

represent the presence of oxygen. We also have good evidence that the emitters are excited MoO molecules formed by simultaneous sputtering of an Mo atom and an excited O contaminant atom. The work has recently been published and I refer you to the attached reprint for details. The abstract of the paper is as follows:

On the Origin of Broad Band Optical Emissions from Mo, Nb and W bombarded by Heavy Ions by E. O. Rausch, A. I. Bazhin and E. W. Thomas. (J. Chem. Phys. 65, 4447 (1976)).

> Continuum emission has been observed when Mo, W and Nb targets were bombarded with 10 to 30 keV, Ne^+ and Ar^+. The emission occurs only when the environment of the target chamber contains an oxygen partial pressure of 2×10^{-9} torr or above; for lower pressures the emission is absent. Identical continua are also observed when the metal oxides are bombarded with Ne^+ and Ar^+; similar spectral features, though with changed relative intensities, are seen when the targets are bombarded with O^+ and O_2^+ ions in the absence of O_2 gas in the vacuum environment. A significant feature of these continua is that the emitting species extend for some mm beyond the bombarded surface. We suggest that the source of the emission is sputtered oxides of the target. The variation of emission intensity with oxygen partial pressure and bombarding ion beam current is consistent with a mechanism where the oxide is formed by the simultaneous sputtering of an adsorbed oxygen atom and a metal atom from the bulk material.

We have surmised that the excited species is a combination of ground state Mo and metastable excited O; the decay is to a repulsive ground state of MoO. This excited system is in many ways analogous to the rare gas halide systems finding recent application for uv lasers. The metal oxide system should also have laser potential and indeed there has recently been a patent issued to ERDA for an MoO* chemical laser device. It is interesting that the excited metal oxide complexes are not readily created in discharge spectra. We believe this occurs because the internuclear separation in the excited molecule is considerably greater than that of the molecular ground state; thus the excited state is not accessible by a direct Franck-Condon transition. This sputtering technique may provide an extensive class of molecular spectra which are not accessible in conventional flame and discharge sources.

An important question which remains to be answered is why does the sputtered oxygen emerge so readily in the metastable state? This may be associated with electronic structure of the oxygen when chemically bonded to the surface.

There would seem to be good reason to expect that chemisorption of other species on metals should also permit production of unusual excited states by sputtering. A survey of other possible combinations has been initiated and we already have evidence of metal carbide molecule formation.

This work has provided some useful information concerning sputtering of chemisorbed species; there is a close correlation between our observation of MoO* and work in SIMS (secondary ion mass spectrometry) where MoO+ ions occur very readily when traces of oxygen are present. We have recently shown that these spectra are also excited by light ion impact (H+); the low signal intensity merely represents the small sputtering coefficients for light ions. Our studies permit us to measure the coefficient for sputtering of chemisorbed oxygen.

B. Luminescence of CN Molecules on Alkali Halides

Early in this project we discovered that light ion (H+) impact on alkali halide crystals gave rise to a molecular band emission. This was due to contaminants and could be readily removed by standard cleaning techniques (e.g. sputtering or heating). We have identified the species as CN and the conclusions have been reported. The paper is attached for your reference and the abstract is as follows:

Ion Induced Luminescence of Alkali Halide with CN Impurtiy, by A. I. Bazhin, E. O. Rausch and E. W. Thomas (J. Chem. Phys. 65, 3897 (1976)).

> During a stydy of luminescence induced by low energy (20 Kev) light ion (H+, He+) impact on certain alkali halides (LiCℓ, NaBr, NaCℓ, KBr, KCℓ) we have observed a band spectrum in the region 230 nm to 350 nm. The bands are separated by 0.26 eV and have a half width of 0.12 eV; no fine structure is observed. Identical bands of much increased intensity are observed when samples deliberately doped with CN are bombarded. The phenomenon is not found with KBr crystals. We suggest that the observed bands are due to transitions in the CN molecule, the $D^2\Pi_1 - X^2\Sigma^+$ transition that is observed as a very weak transition in discharges. The mechanism whereby CN is formed on the samples remains unclear but appears to be influenced by the presence of adsorbed water.

The mechanism whereby CN is formed is not clear to us; it not introduced directly. We have speculated that it is created by an ion induced chemical reaction involving CO_2, N_2 and water. Work to confirm this speculation and to measure reaction rates is included in a proposal for renewal of this grant.

C. Luminescence from Defects in Alkali Halide

We performed a study of luminescence induced by 10 to 30 keV H+ and He+ ion impact on Alakali Halides at temperatures in the range -160 to 200°C. The luminescence has been positively identified as due to electron-defect

(V_3 and V_4 center) radiative recombination. This has been published during the present period and no further work is anticipated. The title and abstract are as follows, and the full paper is attached for your reference.

Luminescence Induced by Ion Impact on Alkali Halide Crystals at High Temperatures (-160 to 200°C) by A. I. Bazhin, E. O Rausch and E. W. Thomas (Phys. Rev. B 14, 2583 (1976))

A study has been made of luminescence induced by 25-keV H^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependance of luminescence, and the effect of bleaching, in KCℓ and KBr. The peak intensity in the luminescent spectrum is independent of temperature from -160 to -70°C, rises to a maximum at about -10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to O_2 we also observe an additional band characteristic of O_2.

D. Proposed Continuation of the Work

The work described under A and B above shows that chemical species may be monitored by their ion induced optical emission; we have detected unexpected chemical species both on the surface (Section B) and sputtered out of the surface (Section A). The work to date has principally involved the identification of species and some qualitative information on the formation mechanisms. The challenge now is to use the characteristic emissions to monitor rates of reaction on the surfaces. This requires a subsidiary measurement of the surface atomic concentration of the elements involved in the reaction; a suitable monitor of relative concentration (and to an extend absolute concentration) can be provided with a simple Auger system. We suggest that an Auger analyzer should be fitted to our system to permit study of how the concentration of a chemical compound formed on the surface is related to presence of the relevant atomic species.

We also intend to study further the excited species formed by sputtering of transition metals carrying adsorbed layers of foreign atoms; a variety of hitherto unobserved molecular species is expected.

These various objectives have been formulated into renewal proposal which is currently under consideration by your office at NSF.

E. Publications

A total of three detailed publications have been produced in this twelve month period; their abstracts are reproduced above in the appropriate section and reprints are attached.

Two papers were given at the APS conference in Atlanta (1976) and the abstracts have been published (Bull. Am. Phys. Soc. 21, 306 (1976) and 21, 438 (1976).

I am currently writing a major review paper on the subject of "Ion Induced Light Emission from Solids" with two co-authors; it is scheduled for publication in a chapter of a book by the North Holland Publishing Company. Our work at Georgia Tech (sponsored by NSF and ERDA) constitutes almost one third of the whole review.

F. Invited Papers

The work at Georgia Tech on ion induced optical emissions from solids has drawn considerable outside recognition; the program includes both the work under the current NSF grant and also an applications oriented ERDA contract. In fact, I would estimate that with the possible exception of one group (Tolk's work at Bell Telephones) we lead the work in this developing field, both in the USA and abroad. As evidence of this leadership I have been asked to give four invited review papers on this subject at conferences; two were given last summer and two are scheduled for the future. The conferences involved are as follows:

(1) Gordon Conference on Particle Solid Interactions (August 1976)

(2) International Workshop on Inelastic Ion-Surface Collisions (Murray Hill, August 1976)

(3) APS Meeting in San Diego (March 1977)

(4) International Conference on Atomic Collisions in Solids (Moscow, September 1977)

G. Personnel Involved in Program

In addition to myself the following scientific personnel have contributed to the program during the past twelve months.

(1) Dr. A. I. Bazhin (Donetsk University, USSR; Exchange Fellow. No cost to grant)

(2) Hirom Inouye (Japan; Exchange Fellow. No cost to grant)

(3) Otto Rausch (Post Doctoral Assistant. No cost to grant)

(4) Mike Murray (M.S. candidate)

(5) James Harriss (Ph. D. Candidate)

(6) Werner Metz (Ph. D. Candidate)

In conclusion I trust that this brief summary of our activities will fulfill the annual reporting requirement under this grant. Please let me know if further information is required.

Yours sincerely,
E. W. Thomas

E. W. Thomas
Professor
(Telephone 404-894-5215)
894-5230

EWT: ve

Attachment

On the origin of broad band optical emission from Mo, Nb, and W bombarded by heavy ions*

E. O. Rausch, A. I. Bazhin,† and E. W. Thomas

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 15 June 1976)

Continuum emission has been observed when Mo, W, and Nb targets were bombarded with 10–30 keV, Ne^+ and Ar^+. The emission occurs only when the environment of the target chamber contains an oxygen partial pressure of 2×10^{-9} torr or above; for lower pressures the emission is absent. Identical continua are also observed when the metal oxides are bombarded with Ne^+ and Ar^+; similar spectral features, though with changed relative intensities, are seen when the targets are bombarded with O^+ and O_2^+ ions in the absence of O_2 gas in the vacuum environment. A significant feature of these continua is that the emitting species extend for some mm beyond the bombarded surface. We suggest that the source of the emission is sputtered oxides of the target. The variation of emission intensity with oxygen partial pressure and bombarding ion beam current is consistent with a mechanism where the oxide is formed by the simultaneous sputtering of an adsorbed oxygen atom and a metal atom from the bulk material.

I. INTRODUCTION

Bombardment of some metals, notably Mo, W, Ta, V, Nb, and Cr, by low energy (10 to 20 keV) noble gas ions gives rise to a continuum optical emission in the visible and ultraviolet region (see Refs. 1–3 and bibliography cited therein). Previous attempts to indentify the emitters resulted in diverse conclusions. For example, Kiyan *et al.*[3] suggested collective excitation of *nd*-shell electrons of sputtered metal atoms with subsequent radiation of a continuous spectrum due to an oscillating *d* shell. Ejected excited atomic clusters were proposed as the source of emission by White *et al.*[2] Kerkdijk[1] concluded that the emitting species are probably excited neutral metal molecules. A similar study with Si by Thomas *et al.*[4] attributed the broad-band emission observed in the ultraviolet region to the SiO molecule. In this paper new experimental evidence is presented which suggests that the continuum emission previously observed with noble gas ion impact on Mo, Nb, and W is due to sputtered metal oxides.

II. EXPERIMENTAL

The apparatus used for this work is essentially the same as that previously described for studies of light emission when ions strike metal surfaces[5]; we shall therefore give only a very brief description here. The ions are formed in an rf discharge source, accelerated and directed onto the target. Light emission from the point of beam impact on the target was viewed by a conventional scanning monochromator (Jarrell–Ash 84-110) observing through a sapphire window. An EMI 6256S photomultiplier tube was used as a detector. The spectra reproduced here have not been corrected for variation in detection sensitivity; the effective spectral range of the studies extended from 250 to 550 nm. The target materials were polycrystalline metal foils of Mo, W, and Nb obtained from the Materials Research Corporation and said to have a purity better than 99.9%. At various times we used targets as received, with mechanical polishing, or with electrolytic polishing; none of the observations reported here were influenced by the preliminary surface treatment. Some studies were performed with oxide samples. In these cases the oxide was obtained as a powder and simply compressed into a pellet for use as a target. The samples were mounted on a standard manipulator by Varian; this provided three axes of translational motion and one of rotation. The angle of ion beam incidence on the target (angle ϕ in Fig. 1 of Ref. 5) was generally kept at 60° to the target surface normal; the monochromator axis was perpendicular to the direction of the incident ion beam so that it usually viewed the point of beam impact on the surface. For certain studies we placed the angle of incidence at −13°. Under these conditions the incident beam is at 13° to the surface normal but the target is turned so that the monochromator views from behind the target; thus the monochromator does not see the beam spot and can only detect emissions from ejected material at a few *mm* from the surface. Between the target and monochromator was a quartz lens set up to give unity magnification. Thus the detected signal came from a field of view defined by the monochromator slit width which was generally 3 mm wide. By translating the target along the axis of the ion beam we were able to record the spatial distribution of the emitting species.

The composition of gas in the target region could be analyzed and measured with a partial pressure analyzer (Ultek model 607). Typical base pressures were 1×10^{-9} torr. A leak valve was provided so that gases could be deliberately introduced into the target chamber; in this way we were able to create adsorbed gas layers on the target surface. At a typical base pressure of 10^{-9} torr the oxygen partial pressure was only 5×10^{-11} torr. The area of the target irradiated by the ion beam was approximately 5 mm^2 and the beam current density was generally about 10 $\mu A/cm^2$.

III. RESULTS AND DISCUSSION

A. Observed spectra

Figure. 1(a) shows the spectrum observed when 23.5 keV Ar^+ ions are incident on a Mo target in the presence of O_2 at a 2×10^{-8} torr partial pressure; the spectrum includes a variety of features extending continuously through the spectral range recorded (250 to

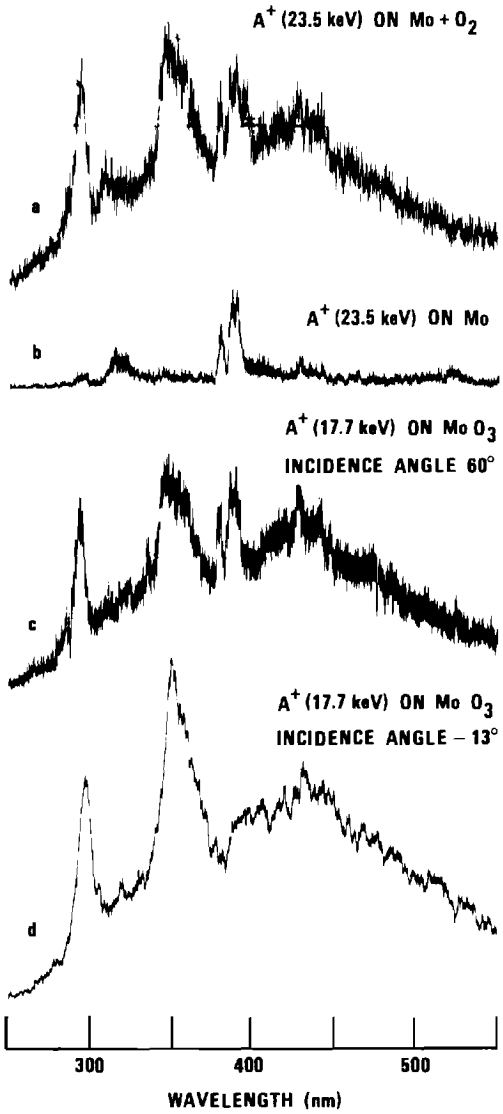

FIG. 1. Spectra recorded for Ar^+ impact on Mo and MoO_3 targets. (a) 23.5 keV Ar^+ on Mo in the presence of 2×10^{-8} torr of O_2. (b) 23.5 keV Ar^+ on Mo at chamber base pressure of 2×10^{-9} torr (oxygen partial pressure of 2×10^{-11} torr). (c) 17.7 keV Ar^+ on MoO_3 at chamber base pressure of 2×10^{-9} torr; taken at an angle of 60° so that the point of beam impact on the surface is viewed. (d) 17.7 keV Ar^+ on MoO_3 at chamber base pressure of 2×10^{-9} torr; taken at an angle of $-13°$ so that the point of beam impact on the surface is not viewed.

550 nm). When the oxygen supply is terminated and the vacuum system returns to a base pressure of 1×10^{-9} torr (5×10^{-11} torr partial pressure of O_2) the majority of the features are no longer present and the spectrum shown in Fig. 1(b) is observed. The previously published work of Kerkdijk *et al.*,[1] and White *et al.*,[2] show spectra which appear to be identical to that of Fig. 1(a) obtained here with deliberate introduction of oxygen. We note that these earlier studies used relatively poor base pressures (2×10^{-8} torr or higher) and we suggest that the observed emissions were related to the presence of oxygen. When oxygen is not present [Fig. 1(b)] the spectrum consists primarily of atomic molybdenum lines in the region of 380–390 nm; and weaker lines around 310 nm; under high resolution they can be resolved and identified. These atomic lines also occur when Mo is bombarded in the presence of O_2 but they are then superimposed on other features. The spectrum recorded with the presence of O_2 [Fig. 1(a)] has the form of a broad underlying continuum extending over the region 250 to 550 nm with a number of broad peaks superimposed on it particulary at 290 and 360 nm. These peaks have been studied with 0.1 Å resolution[1] and have a width of tens of nm but exhibit no structure, so apparently they too are continua but of limited spectral extent. The atomic Mo lines have been identified[1,2] as due to sputtered target atoms and will not be considered further in the present paper. The matter of interest here is the orgin of the continuum and the broad peaks.

Various other spectral recordings have been made to confirm that the underlying continuum and the broad peaks are associated with the presence of oxygen. In Fig. 1(c) we show the observed spectrum with Ar^+ impact on MoO_3; the spectrum is identical with that for Ar^+ on Mo in the presence of O_2. When H_2 or N_2 was introduced into the target cell, the continuum and broad peaks were not observed; Fig. 2(a) shows a recording with H_2 in the chamber. However with the introduction of carbon monoxide onto the Mo target both the continuum and broad peaks appeared again but with a greater intensity than was observed with oxygen; this is shown in Fig. 2(b). The spectrum obtained with CO in the target region shows a discrete line at 426.7 nm which we identify as the $4\,^2F^0 - 3\,^2D$ CII transition in sputtered carbon; it is not present in any other spectra. We performed a variety of tests to determine whether the emitters were in any way related to the nature of the projectile ion. Use of Ne^+ projectile beam gave exactly the same spectrum as Ar^+ when oxygen was present in the target chamber, and only metal atomic line emissions for oxygen partial pressures below 2×10^{-9} torr. Impact of an O_2^+ beam on the Mo target in the presence of oxygen again gave a similar spectrum as for Ar^+ impact; a sample recording is shown in Fig. 2(c). Impact of O_2^+ on Mo in the absence of oxygen gave the spectrum shown in Fig. 2(d) which has the same broad peaks found with presence of oxygen gas but with the underlying continuum either absent or much reduced in intensity. Impact of O^+ ions gave a similar behavior to O_2^+ impact. These various tests suggest that the continuum and the broad peaks are associated with the presence of oxygen on the molybdenum target either as an adsorbed layer or by injection from an oxygen ion beam; the spectral features are not related to the rare gas ions used as the incident species in our experiments and those of others.[1,2]

In the previous work of Kerkdijk *et al.*,[1] and of White *et al.*,[2] it was shown that application of electric fields up to 4000 V/cm did not change the spatial distribution of emitters; similar results were obtained in the present work. Kerkdijk *et al.*[1] have shown that this means the emitters are not charged.

The emission was not confined to the surface, but extended as much as 1 cm in front of the target. Similar observations were reported by Kerkdijk[1] and White.[2]

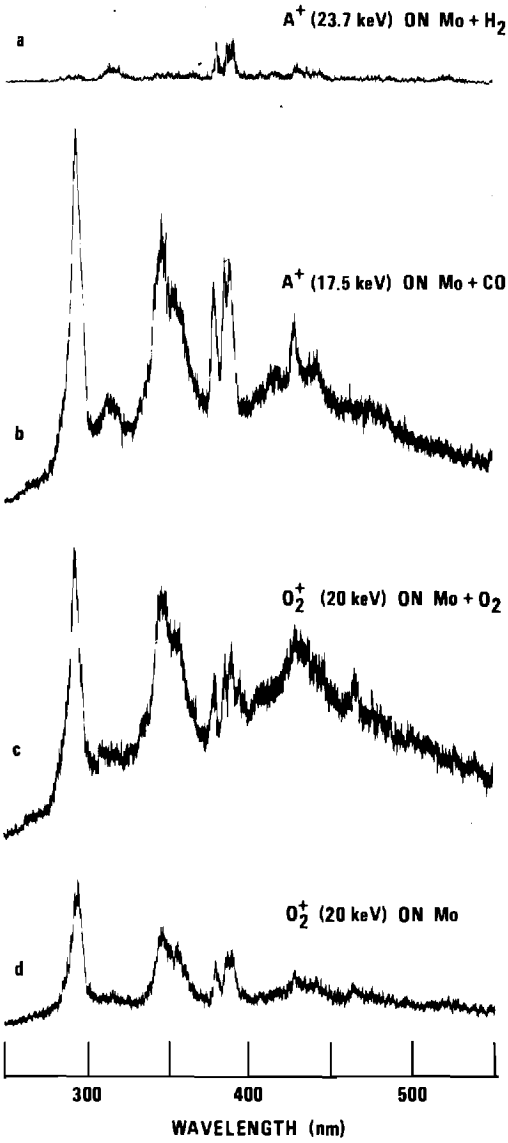

FIG. 2. Spectra recorded for Ar^+ and O_2^+ impact on Mo targets. (a) 23.7 keV Ar^+ on Mo in the presence of 2×10^{-8} torr of H_2. (b) 23.5 keV Ar^+ on Mo in the presence of 2×10^{-8} torr of CO. (c) 20 keV O_2^+ on Mo in the presence of 2×10^{-8} torr of O_2. (d) 20 keV O_2^+ on Mo at the chamber base pressure of 2×10^{-9} torr.

In order to investigate whether the same emission processes were active on, as well as in front of the surface, the target was rotated to an incident angle of -13° such that only radiation from the luminous glow above the surface (at distances >1 mm from the target surface) was recorded. The continua and broad peaks were again observed but the atomic line emissions were absent; a spectrum taken under these conditions with an MoO_3 target is shown as Fig. 1(d). The absence of the atomic lines is expected; if the lifetime of the excited atomic states is about 10^{-8} sec and the velocity (calculated from the most probably energy, ~10 eV, of the sputtered atoms[6]) is about 4000 m/sec, then, most of the atomic line emission occurs approximately 0.05 mm from the surface. Since the energy distribution of the sputtered particles does not significantly change with their mass[6] it is concluded that the lifetime of the emitters giving the continua and broad peaks must be greater than 10^{-6} sec. The fact that the source of emission extends some millimeters in front of the surface indicates that the emission originates from ejected particles; the emission cannot be due to excitations in the solid itself.

We have also recorded spectra using Nb and W targets under heavy ion bombardment. For a high vacuum situation with oxygen partial pressures below 10^{-9} torr, one observes only atomic line emission from sputtered atoms. When O_2 is introduced to a partial pressure of 2×10^{-9} torr or above, we observe intense continua with some broad peaks. Samples of the observed spectra are shown in Fig. 3 and are quite similar to previously published spectra[1,2] taken without deliberate introduction of O_2 but under relatively poor vacuum conditions (base pressure $>2\times10^{-8}$ torr). Again we would conclude that these spectra are associated with the presence of oxygen.

As mentioned above, when no oxygen is present the only significant features observed are atomic lines identifiable as due to sputtered metal atoms. However there remains a very weak signal throughout the spectral region studied. The signal is at the limit of our detection sensitivity and cannot be studied in any detail. In previous studies of clean Al, Cu, Mo, Nb, and W bombarded by light ions (H^+ and He^+) a weak continuous emission has been observed[7,8] which in one case (Al) has been identified as due to electron–hole radiative recombination in the solid.[8] The source of these weak emissions is located in the solid and they do not exhibit the substantial spatial extent of the continuum and broad bands observed when Mo is bombarded in the presence of O_2. We believe that they may be due to electron–hole recombination effects in the solid. Such emissions will be referred to as the "residual back-

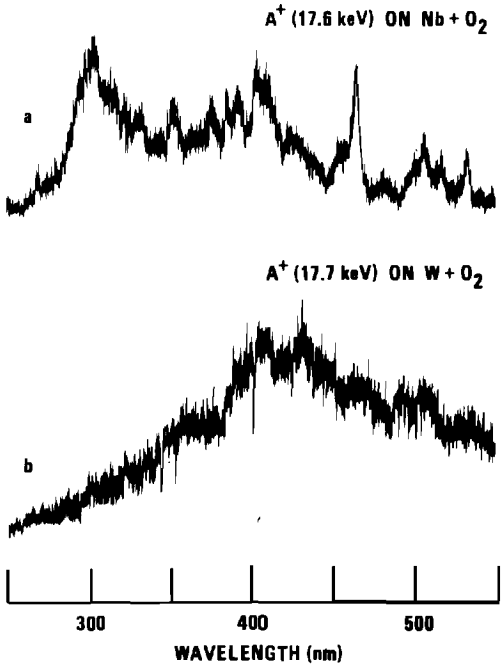

FIG. 3. Spectra recorded for 23.7 keV Ar^+ impact on Nb and W in the presence of 2×10^{-8} torr of O_2.

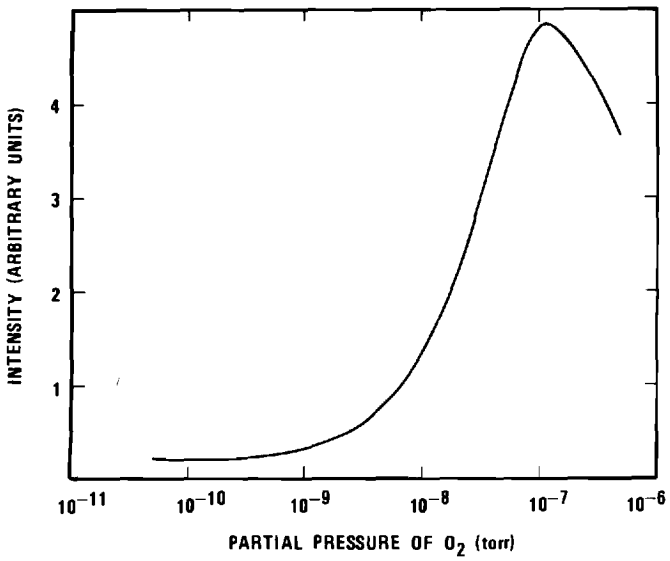

FIG. 4. Emission intensity at 296 nm as a function of oxygen partial pressure when an Mo target is bombarded by 23 keV Ar^+ at a current density of approximately 10 $\mu A/cm^2$.

ground" and its origin will not be discussed further.

The foregoing results confine the search for the nature of the species emitting the continua and broad peaks to the following species:

(a) A neutral metal complex M_n.

(b) A neutral oxygen complex O_n.

(c) A neutral metal–oxygen molecular complex M_nO_n.

It is well known that a heavy ion beam, such as Ar^+, will eject significant fluxes of charged atomic clusters from metals.[6,9,10] Consequently we should consider the possiblity that excited neutral metal complexes of the form M_n^* are being ejected. We did observe excited metal atoms under all conditions, whether oxygen was present or not. There is no reason to believe that multimers should behave in a significantly different manner from the monomer and require the presence of oxygen for formation. Thus we believe that the absence of continuum emission at low oxygen pressures indicate that the excited specie is not the metal complex M_n^*. Bombardment of tungsten surfaces exposed to oxygen is known to produce sputtered O_2^+,[10] and it is conceivable that the continuum emission observed here might be due to sputtered excited oxygen complexes, O_n^*. If oxygen were a significant contributer to the emission one would expect to observe similar spectra for Mo, Nb, and W targets; apart from an apparent broad underlying continuum extending over the whole spectral range there is no similarity between the three cases. Moreover, there is extensive experience with the spectra of oxygen and the most recent comprehensive review[11] lists no known emission continua. We therefore conclude that the significant features of the observed spectra are probably not due to O_n^*.

The elimination of metal or oxygen complexes leaves only the metal oxygen complex M_nO_n as possible sources of the emission. It is well known[10] that sputtering of a metal covered with adsorbed oxygen gives rise to secondary metal oxide ions and that sputtering of metal oxides gives rise to substantial fractions of ejected neutral metal oxide molecules.[12,13] The fact that ion impact on MoO_3 gives an identical spectrum to that observed for ion impact on Mo in the presence of O_2 suggests strongly that the metal oxide is involved. We shall now proceed to examine the behavior of the observed emission spectra on the assumption that they are indeed due to a metal oxide. We shall concentrate on the spectrum observed with Mo targets.

B. Dependance of intensity on pressure and beam current

On the assumption that the emitters are indeed metal oxide molecules, we shall now examine how the emission intensity should depend on oxygen pressure and beam current. Our experimental data on pressure and beam current dependance for Mo targets are shown in Figs. 4–6. Figure 4 shows the dependance on oxygen partial pressure of the intensity at 296 nm; this is a distinct broad peak. Figure 5 shows the intensity at 325 nm; this wavelength is a point in the general underlying continuum which stretches over the whole observed spectral region. These two figures show that below 2×10^{-9} torr the intensity is small and independent of oxygen partial pressure; this is not due to ejected particles and has been referred to earlier as the residual background. For pressures above 2×10^{-9} torr the intensity rises steeply to about 10^{-7} torr. At higher pressures the intensity of the 296 nm emission decreases with increasing pressure. In contrast, the underlying continuum observed at 325 nm saturates at 10^{-7} torr and does not decrease appreciably at higher pressures. Figure 6 shows intensity as a function of projectile beam current for various points in the spectrum; all recordings show a linear dependance.

A satisfactory theory for sputtering of dimers and other clusters has been given by Können *et al.*[14] They suggest that a single incident projectile sputters two or more target atoms which leave the target at the same time and for which the sum of potential energy and rela-

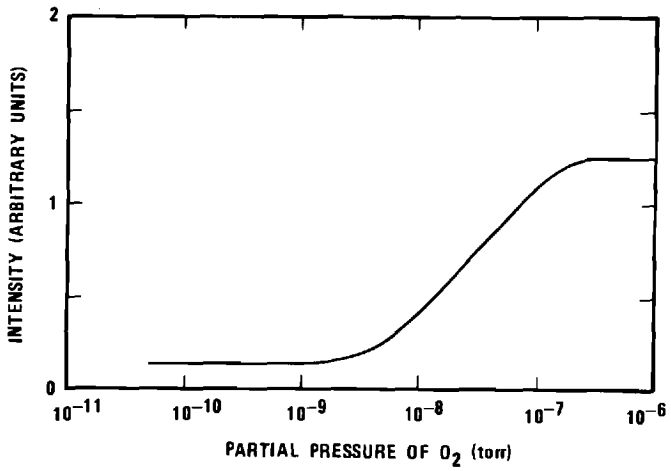

FIG. 5. Emission intensity at 325 nm as a function of oxygen partial pressure when an Mo target is bombarded by 23 keV Ar^+ at a current density of approximately 10 $\mu A/cm^2$.

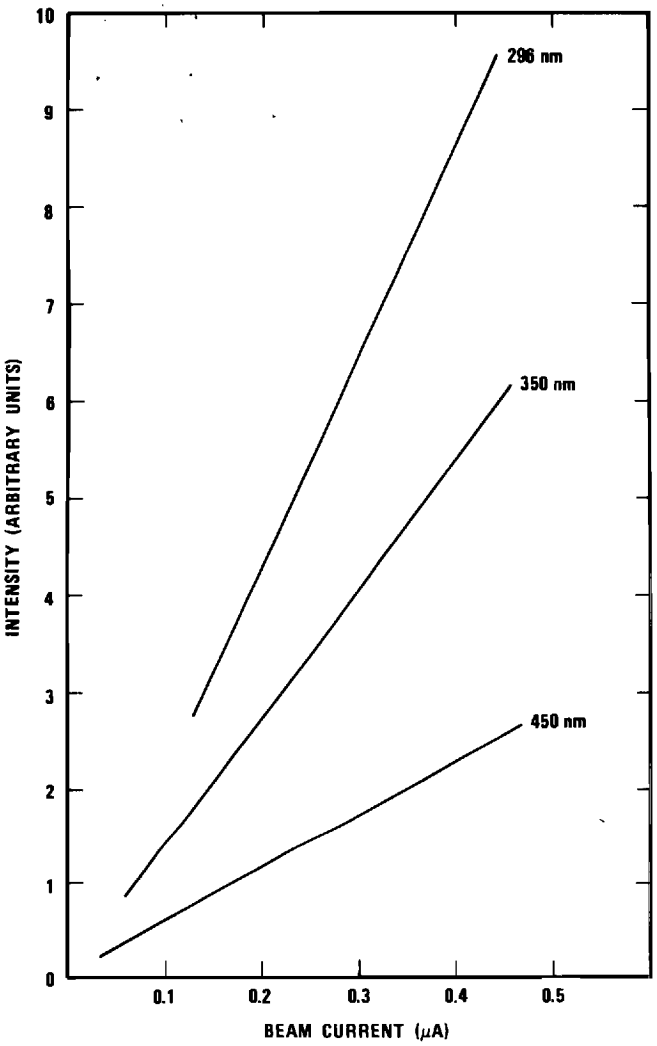

FIG. 6. Emission intensity at 296 nm, 350 nm and 450 nm as a function of projectile beam current for 23 keV Ar^+ bombardment of Mo in the presence of O_2 at a partial pressure of 4×10^{-8} torr.

tive kinetic energy does not exceed the dissociation energy for the cluster. We assume that the same mechanism can be invoked to explain formation of sputtered metal oxides. The metal atom comes from the target surface and the oxygen from an adsorbed layer on the surface; if the energy criterion of Können *et al.*[14]; is fulfilled then the sputtered atoms emerge together as a molecule. Excited molecules will be formed if one or both of the sputtered species are excited.

A continuous emission spectrum will occur if the molecule decays radiatively to a repulsive lower state; if the lower state is only weakly repulsive at the relevant internuclear separation then the continuum emission will have the form of broad peaks. In modelling the rate at which the sputtered oxides are formed we are of course dealing with a dynamic situation since oxygen is being continually removed by sputtering and continually replaced by oxygen arriving from the surrounding environment.

The emission intensity must depend on a number of factors such as the sputtering coefficients of the metal and of the adsorbed oxygen, the sticking probability of oxygen and the rate at which metal and oxygen atoms are simultaneously sputtered. The latter, in turn, depends on the oxygen coverage of the metal surface. An increase in oxygen coverage is expected to result initially in an increased sputtering of oxides and hence an increase in photon emission. However, as surface coverage increases the yield of metal atoms should decline.

The concentration of oxygen atoms on the surface is given by[15] the following equation:

$$\frac{dN_O}{dt} = -\frac{I_B S_{Ox} N_O}{N_M} + P_A \sigma. \tag{1}$$

Here N_O is the density of oxygen on the surface, I_B the beam flux density (ions/cm^2 – sec), S_{Ox} the sputtering ratio of oxygen, N_M the atomic surface density of the metal, P_A the number of oxygen atoms arriving per unit time from the surrounding gas, and σ is the sticking probability. The solution to this equation is that N_O decays exponentially with time so that at large times (where dN_O/dt tends to zero) the solution becomes

$$N_O = N_M \frac{P_A \sigma}{I_B S_{Ox}} \tag{2}$$

We shall write the equilibrium value N_O/N_M as f_{Ox}, the fractional surface coverage of oxygen. The sticking coefficient will be taken as constant and having a value of unity[16]; this assumption is valid only for low surface coverages[16] and clearly restricts the applicability of our results to low pressures.

To estimate the rate of metal oxide formation by sputtering (as an example we use molybdenum oxide) we need the rate of oxygen sputtering

$$R_{Ox} = S_{Ox} f_{Ox} I_B \tag{3}$$

and the rate of molybdenum sputtering

$$R_{Mo} = S_{Mo}(1 - f_{Ox}) I_B. \tag{4}$$

Here S_{Mo} is the sputtering ratio for Mo ejection and it is assumed that the molybdenum sputtering is proportional to the fraction of the surface not covered by oxygen (i.e., $1 - f_{Ox}$). The rate of metal oxide sputtering, and hence of photon emission will be given by I such that

$$I \propto R_{Ox} R_{Mo} = [S_{Ox} f_{Ox} I_B][S_{Mo}(1 - f_{Ox}) I_B] F. \tag{5}$$

The factor F represents the probability that two ejected atoms will recombine to form an excited state and emit a photon; this factor is unknown and is assumed to be constant. Thus the observed intensity is proportional to $f_{Ox}(1 - f_{Ox})$. Inserting f_{Ox} from Eq. (2) into Eq. (5) we arrive at

$$I = S_{Ox} S_{Mo} F I_B^2 \left[\frac{P_A \sigma}{I_B S_{Ox}}\right]\left[1 - \frac{P_A \sigma}{I_B S_{Ox}}\right]$$

$$= F S_{Mo} \left\{P_A \sigma I_B - \frac{P_A^2 \sigma^2}{S_{Ox}}\right\}. \tag{6}$$

Since P_A is proportional to the partial pressure of oxygen, p, this equation predicts that photon intensity divided by p^2 should vary linearly with $1/p$. Figure 7

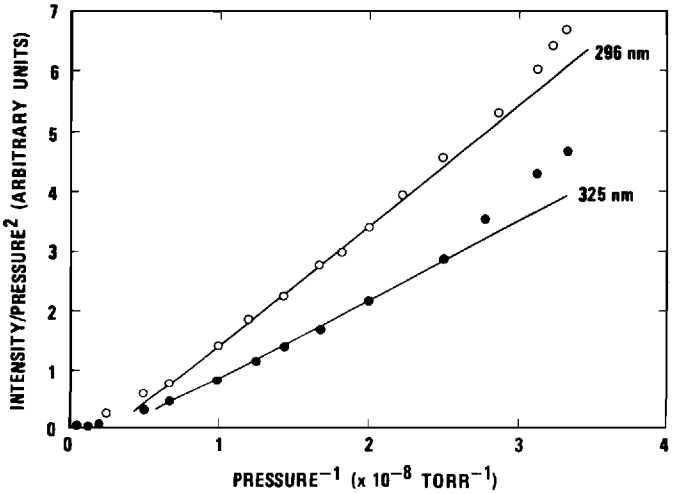

FIG. 7. Plot of I/p^2 (Intensity divided by oxygen pressure squared) against the reciprocal of oxygen pressure. Data are taken from Figs. 4 and 5.

shows such a plot for emissions at two wavelengths. Linearity is indeed observed up to a pressure of about 2×10^{-8} torr. At higher pressures the plot is nonlinear, but this simply represents the fact that the sticking coefficient will vary at high surface coverages and will approach zero. The divergence from linearity at low pressures is due to the residual background that has been discussed earlier. According to Eq. (6) the intercept of the linear portion with the pressure axis will occur when $P_A = I_B S_{Ox}/\sigma$. P_A is the rate of atom arrival at the surface and is simply $2(M\bar{v}/4)$, where N is the number density of gas molecules, $\bar{v}$ is their mean thermal velocity, and the factor 2 is included to allow for the fact that oxygen is diatomic. Taking the pressure at the intercept and assuming the sticking coefficient is unity, we would get an oxygen sputtering coefficient, S_{Ox}, of about 0.4. Equation (6) also predicts intensity to vary linearly with beam current density; the data of Fig. 6 are in accord with this prediction.

Thus the observed intensity, as a function of pressure and beam current, is consistent with our model for formation of MoO* by simultaneous sputtering of Mo and O. Sputtering of metal complexes Mo_n would be predicted to behave like $(R_{Mo})^n$ from Eq. (4) and sputtering of oxygen complexes O_n should behave like $(R_{Ox})^n$ from Eq. 3. The fact that the observed intensity does not behave like these functions is a further indication that sputtering of oxygen or metal complexes is not the source of the emission.

This development proceeded on the assumption that a single Mo atom and single O atom were sputtered to create MoO*. The same arguments would hold if oxygen were both adsorbed and sputtered as the diatomic molecule O_2 leading to formation of MoO_2^*.

We have also studied the emission from MoO_3 bombarded by Ar^+ in the presence of oxygen; the data are shown in Fig. 8. Emission at 325 and 425 nm is from the broad underlying continuum that extends throughout the observed spectral region while the 296 nm emission is at the intense sharp peak. We note that the 325 and 425 nm emissions are essentially independent of pressure. This is to be expected since oxygen is present in the target and we do not have to rely on adsorbed oxygen from the surrounding gas. The emission of the 295 nm peak is independent of oxygen pressure up to 4×10^{-8} torr then falls with increasing pressure. We recall that such a decrease at pressures above 10^{-7} torr occurs also for the same band generated when Ar^+ bombards Mo in the presence of O_2. This decrease is not due to collisional destruction of MoO* since measurements analogous to those of Fig. 8 but with argon introduced into the target cell instead of O_2, gives no pressure dependance at any of these wavelengths. Thus at oxygen pressures above 10^{-7} torr the behavior of emissions from MoO_3 and from Mo in the presence of O_2 are identical.

It remains unclear as to why the emission as a function of oxygen pressure behaves differently at the 296 nm peak and the 325 nm underlying continuum when pressures are above 10^{-7} torr. The simple two component sputtering model described above is probably not applicable at these relatively high pressures and provides no clue. Undoubtedly, the difference in behavior indicates that the emitting states contributing at these wavelengths are not the same.

C. Time dependence of intensity

When a target is exposed to oxygen without the presence of the ion beam the oxygen coverage will increase to some equilibrium value; if now the ion beam is returned to the target there is a reduction of surface coverage due to sputtering and eventually a new equilibrium coverage is established where the rate of removal by sputtering is equal to the rate of arrival of oxygen from the gas. Surface coverage as a function of time will be given[15] by the solution of Eq. (1)

$$N_O = \frac{P_A \sigma N_M}{I_B S_{Ox}} + C\exp\left(-\frac{I_B S_{Ox} t}{N_M}\right), \tag{7}$$

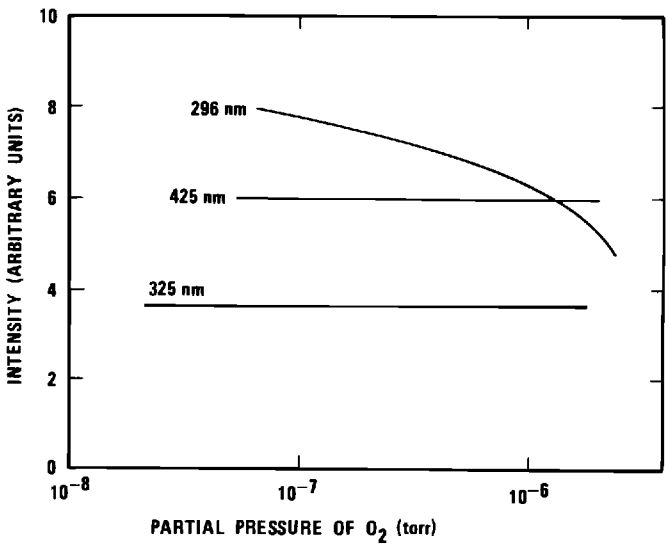

FIG. 8. Emission intensity at 296 nm, 350 nm, and 425 nm as a function of oxygen partial pressure for Ar^+ bombardment of MoO_3 in the presence of O_2.

C being an integration constant. Thus the oxygen surface coverage f_{Ox} should decrease exponentially with time towards an equilibrium value of:

$$f_{Ox} = \frac{P_A \sigma}{I_B S_{Ox}} \quad . \tag{8}$$

A temporal decay of emission intensity was, in fact, observed when an ion beam was first directed onto a target with oxygen already present. An increase of intensity with time was observed when oxygen was introduced for the first time to a target with the ion beam present; this is in accord with Eq. (7) if the boundary condition $N_O(t=0)=0$ is employed to establish the constant C. At long times the intensity becomes stable corresponding to the equilibrium surface coverage given by Eq. (8). All the data presented in this paper were in fact taken under conditions where emission intensity had become independent of time.

From Eq. (7) the time constant for establishment of equilibrium conditions is $N_M/I_B S_{Ox}$. Experimentally the time constant for establishment of constant intensity was of the order 60 sec which implies a value for S_{Ox} of approximately 0.4. The temporal variation is completely consistent with the model described in the preceding section and the value of S_{Ox}, the oxygen sputtering coefficient, derived therefrom is consistent with the value determined from the pressure dependance of emission intensity.

For the emission induced by Ar^+ bombardment of MoO_3 we found the intensity to increase by a factor of two during a time period of approximately one half hour, which corresponded to an Ar^+ bombardment dose of 2×10^{17} ions/cm^2. Naguib and Kelley[17] have shown that bombardment of MoO_3 to this dose level causes reduction of MoO_3 to the lower oxide MoO_2. This observation is a further indication that the continuum emission probably originates from one of the lower oxides MoO or MoO_2 and not from MoO_3. The measurements of intensity induced by Ar^+ on MoO_3 as a function of oxygen pressure (Fig. 8) were taken after a considerable period of bombardment when the intensity had attained a constant value.

D. Spatial distribution of emitters

The continuum emission from Mo, Nb, and W targets is observed to extend many mm in front of the bombarded surface. Kerkdijk *et al.*[1] have made detailed measurements of this spatial dependance for the case of Ar^+ incident normally on Mo. If the ejected particles emerge perpendicular to the surface, then the intensity will decrease exponentially with distance x according to the equation $I=I_0 \exp[-(x/v\tau)]$; here τ is the excited state lifetime and v is the emitter velocity. Analysis of Kerkdijk's data[1] for Ar^+ on Mo, under this assumption, shows the emission intensity decay to consist of two compoents with $v\tau$ values of 1.07 and 6.04 mm, respectively. If one assumes that a single velocity v of 4100 m/sec is appropriate to the sputtered particles[6] then the decay curves lead to lifetimes of 2.6×10^{-7} and 1.5×10^{-6} sec, respectively. Our own measurements also lead to a lifetime estimate of 1×10^{-6} sec for the longer lived component. This lifetime is obtained both at the broad peak (296 nm) and for the underlying continuum (325 nm).

E. Nature of the emitting state

Continuous molecular emission spectra occur by transitions to a repulsive lower state. There appears to be no definitive identification of the MoO spectrum in conventional sources. Weak line emissions, tentatively attributed to the monoxide, have been listed[18] and the spectrum does exhibit strong continua in the visible region. There are other fragmentary references to the continuum emission from this oxide. For example it was reported that the molybdenum oxide continuum peaks in intensity at 400 nm[9]; our spectra shown in Figs. 1 and 2 peak at approximately 420 nm. We must conclude that a continuous spectrum is to be expected from MoO and indeed has been previously observed in conventional spectroscopic sources. Presumably, the above arguments can be extended to include tungsten and niobium, although these metals were not investigated as extensively as molybdenum.

In molybdenum spectra of Figs. 1 and 2 there is a peak at 296 nm that would appear to be rather narrower than one would expect from a transition to a repulsive state. However, similar narrow "continua" have been observed in the decay of rare gas–halide molecules and Golde[20] has shown how these can arise if the ground state potential energy curve is almost flat.

Any attempt to identify the precise nature of the emitting species must be speculative and based only on the present experimental observations. A model of excited oxide formation by separate sputtering of metal and oxygen atoms would require that some excited atoms escape and radiate as atoms; thus an observed atomic line spectrum would provide a clue as to the nature of the excited molecular states which could be formed. Lines from sputtered metal atoms are seen in the absence of oxygen but their intensity is collectively many orders of magnitude less than that of the integrated continuous spectrum; thus association of excited metal atoms with oxygen is unlikely to be the principal source of the band emission. Also we see no atomic lines of oxygen. However it is possible that the continuum emission results from MoO* formed by association of Mo with metastable oxygen atoms. For example MoO* might be formed from ground state metal atoms and the $O(2p^4\,{}^1S)$ metastable state. If the MoO* is formed in a high vibrational level and decays to a repulsive $Mo+O(2p^4\,{}^3P)$ ground state then emission should be close to the $2p^4\,{}^1S \rightarrow 2p^4\,{}^3S$ photon energy which gives a wavelength of 296 nm; this is at the relatively sharp peak shown here in Fig. 1 and 2. Moreover, since the $O(2p^4\,{}^1S)$ is metastable, the corresponding molecular transition should also be long lived. Finally, the $2p^4\,{}^1S \rightarrow 2p^4\,{}^3P$ transition in O has two decay paths corresponding to the $J=1$ and $J=2$ configurations of the ground state; thus two relatively long lived decays should be observed which is consistent with our analysis of the spatial distribution given by Kerkdijk *et al.*[1,2]

III. CONCLUSION

We have shown quite unabiguously that continua and broad peaks observed when Mo, Nb, and W are bombarded with heavy ions are associated with presence of oxygen at a partial pressure of 2×10^{-9} torr or above. Previous studies of these spectra were performed[1,2] with relatively poor vacuum conditions where one would expect that considerable oxygen was always present. The experimental observations suggest that the broad peaks and continuum in the case of Mo is from excited MoO. This molecule is produced by simultaneous sputtering of a metal atom and an adsorbed oxygen atom such that the sum of the total potential energy and relative kinetic energy does not exceed the dissociation energy of the molecule; this model is consistent with an established theory of cluster formation.[14] We speculate that the molecular state is formed from a ground state metal atom and a metastable oxygen atom. However, it must be admitted that the experimental data presented here does not conclusively prove that higher oxides, such as MoO_2 and MoO_3, do not contribute to the emission. Indeed, the differences between pressure dependance of the 296 nm broad peak and the underlying continuum measured at 325 nm (see Figs. 6 and 8) suggests that two different mechanisms for excited oxide formation might be present.

Ion beam bombardment of certain metal oxides, or of metals with adsorbed oxygen, would appear to facilitate spectroscopic studies of molecular systems not readily accessible in conventional spectroscopic sources.

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†Soviet Scholar sponsored by the USA/USSR young faculty exchange program. Permanent address: Dept. of Physics, Donetsk University, Donetsk, Ukraine, USSR.

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Ion induced luminescence of alkali halides with CN impurity*

A. I. Bazhin,† E. O. Rausch, and E. W. Thomas

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 15 June 1976)

During a study of luminescence induced by low energy (20 keV) light ion (H^+, He^+) impact on certain alkali halides (LiCl, NaBr, NaCl, KBr, KCl) we have observed a band spectrum in the region 230 to 350 nm. The bands are separated by 0.26 eV and have a half-width of 0.12 eV; no fine structure is observed. Identical bands of much increased intensity are observed when samples deliberately doped with CN^- are bombarded. The phenomenon is not found with KBr crystals. We suggest that the observed bands are due to transitions in the CN radical, possibly the $D\,^2\Pi_i - X\,^2\Sigma^+$ transition that is observed as a very weak transition in discharges. The mechanism whereby CN is formed on the samples remains unclear.

I. INTRODUCTION

In performing studies of luminescence induced by impact of light ions (H^+ and He^+) at low energies (20 keV) on certain alkali halide crystals (LiCl, NaBr, NaCl, KBr, KCl) we have in some cases observed an emission band structure peaking at 270 nm that has the appearance of a molecular vibrational structure. The purpose of this paper is to suggest that the species which gives rise to this band is the CN radical.

The experimental arrangement for this work has been described elsewhere[1,2] and we shall provide only a brief description here; a sketch of the apparatus is provided as Fig. 1. The projectile ions are produced in an rf source, accelerated, mass analyzed, and directed onto a single crystal of the target material. Ions are incident at an angle of 45° to the target surface normal and the light emission from the point of impact is analyzed by a scanning monochromator that views the target at right angles to the incident beam direction. The targets are in a 10^{-9} torr ion-pumped vacuum environment and can be cleaned *in situ* by heating or by sputtering with an Ar^+ beam from the accelerator. Some experiments were performed with alkali halide target materials of "optical purity" obtained from the Harshaw Chemical Company, but the majority of the observations utilized samples provided by the Naval Research Laboratory with quoted impurity levels of a few ppm.

II. OBSERVED SPECTRA

Our early observations were of the ion-induced spectrum for He^+ impact on NaCl crystals obtained from the Harshaw Chemical Company; these crystals had been exposed to air for prolonged periods and undoubtedly had accumulated substantial adsorbed impurities from the air. The observed spectrum was essentially the same as that indicated as line (a) in Fig. 2. The broad band peaking at 450 nm has been identified[2] as due to electron recombination with V_3 centers; the broad band peaking at 530 nm has been identified[2] as due to luminescence of O_2^-. The atomic line emission at around 589 nm is the Na–D doublet from sputtered sodium. Of interest in the present paper are the nine intense peaks in the range 210 to 350 nm. As can be seen in Fig. 2, the ultraviolet spectrum in the 210 to 350 nm region consists of well separated bands with essentially constant energy separation ($\Delta E \approx 0.26$ eV) and a half-width of 0.12 eV. Studies with resolutions of 0.1 nm show no structure to the bands. After annealing the sample in vacuum to 420 °C for 1 h, the uv luminescence bands disappeared completely and gave a spectrum similar to that shown in curve (b) of Fig. 2; it will be noted that the annealing procedure also substantially reduces the peak at 530 nm, which we ascribe to O_2^- ions. These observations suggest that the ultraviolet bands must be ascribed to an adsorbed impurity.

All subsequent experiments were performed with the high purity samples, which were freshly cleaved before introduction into the vacuum system. For such a NaCl sample the uv band structure was initially weak or absent. Annealing to 420 °C removed all traces of the uv band spectrum. In order to regain the uv spectrum we studied the effect of exposing the annealed target to various gases in order to simulate the effect of adsorbed impurities. Exposure to air, H_2, N_2, O_2, and CO_2 at 10^{-3} torr did not generate the uv band spectrum. Exposure to cyanogen did produce a spectrum when the target was subsequently bombarded. In this case the emission intensity decreased with time at a rate consistent with the removal by sputtering of a surface layer. We also exposed the target to the vapor of deionized water; in this case there may also have been a substantial amount of air introduced at the same time. The

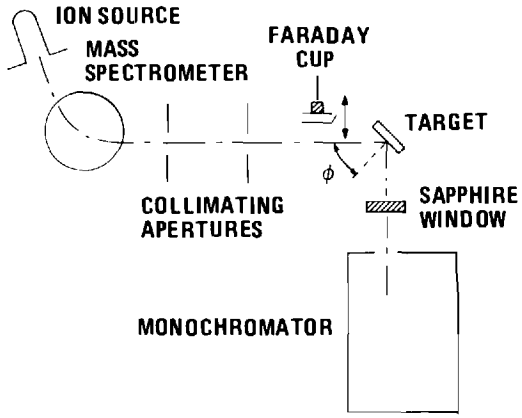

FIG. 1. Schematic diagram of the apparatus.

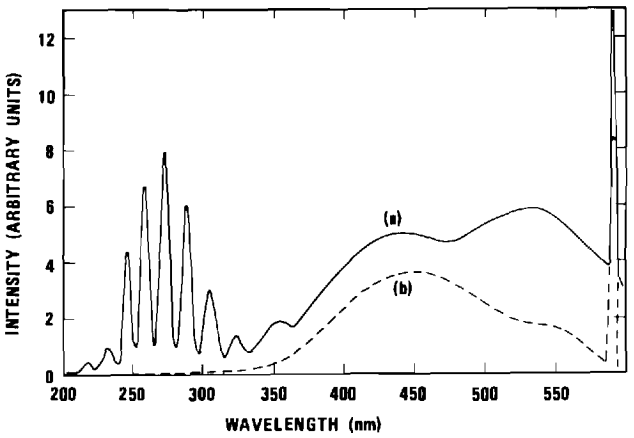

FIG. 2. Luminescence spectra induced by impact of a 20 keV He^+ ion beam of 10 $\mu A/cm^2$ current density on a sample of NaCl held at 26 °C. Line (a) is for the crystal after exposure to H_2O vapor at 10^{-3} Torr at a temperature of 260 °C. Line (b) is for the same sample after a subsequent annealing to 450 °C.

water treatment also caused the production of the uv bands. Figure 2 shows the spectrum observed from NaCl bombarded by He^+; spectrum (a) shows the bands observed after exposure to H_2O while spectrum (b) is for the same crystal after annealing to 450 °C for 1 h followed by cooling to room temperature, and here the bands are absent. These observations are common to LiCl, NaBr, NaCl, and KCl samples; for KBr samples we were unable to generate these uv bands.

For the target materials where these uv bands are produced we find the same spectral characteristics of peak position, peak width, and relative intensity of peaks; the characteristics are the same for H^+ and He^+ impact. With varying target temperature the peak positions and widths are unchanged but the intensity varies quite markedly; Fig. 3 shows the intensity of the 273 nm peak as a function of target temperature for the NaCl crystal from which spectrum (a) in Fig. 2 was generated. This temperature dependence also was essentially the same for all crystals which showed the uv band structure.

III. DISCUSSION

The spectra observed here have the character of a vibrational structure in a molecular transition. The peak separation is in essential agreement with the spacing of vibrational levels in the ground state of CN (2069 cm^{-1}).[3] The breadth of the peaks indicates that the responsible molecular states are severely perturbed; this indicates that the responsible molecular state is either strongly bound to the crystal surface or is perhaps located at an interstitial site within the crystal lattice. We cannot accurately compare these relatively broad bands with the sharp spectra of an isolated molecule. However, we would note that weak bands ascribed to CN have been observed[4] in discharges with band heads at 288 and 274 nm and therefore in good coincidence with the bands observed here; these previously observed bands are very weak and have considerable rotational complexity. They are ascribed to the 0, 10 and 0, 9 transitions in the $D^2\Pi_1 - X^2\Sigma^+$ system of CN. The bands we observe here are consistent with being other components of this same system.

The spectra observed here are identical to the ultraviolet-induced fluorescence bands of NaBr doped with CN^- as recently described by Von der Heyden and Fischer.[5] As a further test of the origin of these bands, we perfomed some studies of ion-induced luminescence of KCl and KBr targets containing CN^-. Such targets were prepared by mixing 0.1% by weight of KCN with KBr or KCl in a finely powdered form and compressing the mixture into a tablet. The spectra induced by ion impact on KCl:KCN showed the same uv band structure as before but now some two orders of magnitude greater in intensity than the visible emission bands. The KBr:KCN target showed only a very weak uv emission of approximately one tenth the intensity of the visible bands; we would recall that the uv spectrum was not found for the supposedly pure KBr samples; neither was it found[5] in the uv induced fluorescence of KBr doped with CN^-. For control purposes we also fabricated pure KCl and KBr samples from the powder and found only very weak uv band emissions in the case of KCl and none for KBr. Samples created from the powder did exhibit an emission peak at around 3100 Å which is presumably due to the well-known OH^- radical.[6] This OH^- peak coincides with one of the uv peaks under discussion here and is identifiable only when the uv band structure is weak or absent; in all cases the OH^- peak could be readily removed by annealing at 250 °C.

Based on the following evidence we suggest that the uv band structure is due to a transition in a molecule containing CN:

(a) The band spacing is appropriate to the ground state vibrational level spacing of CN and certain lines are at[4] positions ascribed to the $D^2\Pi \rightarrow X^2\Sigma^+$ transition of CN.

(b) The spectrum is seen in the ultraviolet-induced fluorescence[5] of alkali halides doped with CN^-.

(c) The spectrum is found in ion-induced luminescence of mixed KCl:KCN samples.

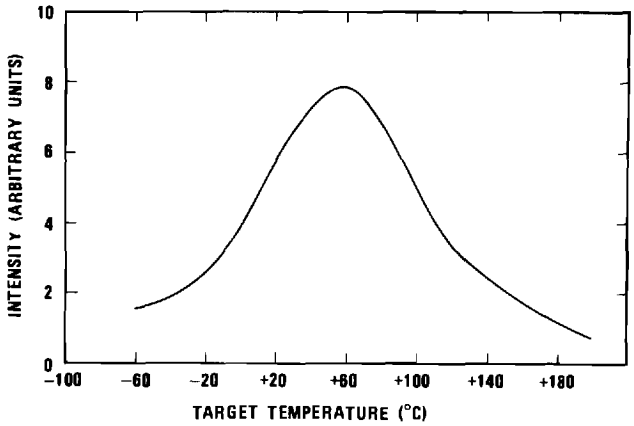

FIG. 3. Temperature dependence of the intensity at 273 nm for the cyrstal from which line (a) in Fig. 2 was generated.

(d) The spectrum may be generated by exposure of a crystal to C_2N_2.

We believe also that the CN is located close to the sample surface for the following reasons:

(a) The projectile ions utilized here penetrate only some 1000 Å, so species at greater depths would presumably not be excited.

(b) The species which gives rise to the bands can be removed by annealing to 450 °C.

(c) The bands can be generated by adsorption of C_2N_2 on the surface.

We see no evidence that the emission is due to a simple CN molecule. A CN^- ion at a substitutional lattice site would be expected to exhibit sharpening of the spectral lines at low temperatures with evidence of phonon structure as has been seen for O_2^- and OH^-[6,7]; this we do not observe at temperatures down to −100 °C and neither is it observed by Von der Heyden and Fischer[5] at 4 °K. Moreover the emission of interstitial CN^- should show small frequency shifts in different lattice materials; no such shift is observed here. We suggest that the CN radical is in a chemically bonded state close to the surface.

In situations where a cyanide or cyanogen is not chemically introduced into our specimens it is unclear where the species come from. The pure crystals are said[8] to have no detectable concentration of cyanide. Our work has shown that simple exposure of the structure to pure gases separately containing C and N does not induce the effect. Certainly carbon is present in the vacuum system as CO and hydrocarbons. Nitrogen is also present in small quantities and certainly will be present as an adsorbed layer on crystals that have been exposed to air; also in our tests performed with water we undoubtedly introduced some nitrogen. It is known[9] that irradiation of gas phase N_2–hydrocarbon mixtures with ultraviolet light or electrons causes fromation of HCN; a similar reaction may be occurring on the crystal surface under ion bombardment.

We offer no explanation of the observation that the bands are produced by introduction of water vapor. Air is introduced with the water but this would seem to be unimportant since dry air alone does not cause the bands. This observation, taken in isolation, might seem to imply that the bands are related to water. However, there is no supporting evidence for such an identification, and we reject it. The effects observed with introduction of H_2O are not understood.

We would argue that the CN emission is not due to direct collisional excitation of the CN radical; if direct excitation were occurring then the emission intensity should not be dependent on target temperature. It seems more likely that the projectile causes formation of excited electron states within the solid and that these subsequently migrate to the surface and decay with the transfer of energy to the CN radical. The temperature dependence of the emission intensity would then simply mirror the stability and mobility of the relevant excited center. A CN radical on the surface may form a local acceptor level in the forbidden zone of the alkali halide and an electron could be captured from the valence band to form CN^-. The rising portion of the temperature dependence (Fig. 3) may represent thermal excitation of this capture and indicates an activation energy of approximately 0.1 eV; thus, the ground state of CN is close to the valence band. The decreasing intensity above 60 °C may indicate recombination of CN^- with valence band holes which become mobile at these temperatures. With this argument the maximum emission of radiation at 60 °C may simply represent the maximum surface coverage by the chemisorbed negative ion.

It is interesting that the uv band spectrum is not observed for any treatment of the pure KBr samples and only very weakly when KBr and KCN are mixed. A plausible mechanism for the source of excitation energy is the recombination of exitons, a mechanism which will liberate an amount of energy appropriate to the band gap. As shown by absorption measurements,[5] the minimum energy for excitation of CN^- in KCl is about 6.9 eV above the ground state and for NaCl the energy is 7.0 eV. For most of the crystals studied here the band gap exceeds the excitation energy of CN^-; for LiCl, NaCl, KCl, the band gaps are, respectively,[10] 8.67, 7.96, and 7.79 eV. By contrast the band gap for KBr is only 6.71 eV and the exiton recombination energy would be insufficient to excite CN^-.

IV. CONCLUSION

The ion-induced luminescence of certain alkali halides with contaminated surfaces exhibits a molecular band structure. A similar but far more intense spectrum is observed when CN is deliberately introduced into the sample. The bands are consistent with the $D^2\Pi_1$–$X^1\Sigma^+$ transition of CN. The breadth of the observed bands suggests that they are located at the crystal surface or at an interstitial site. We conclude that the observed emission is from CN radicals at the surface. It is not yet clear how the species arise from common contaminants.

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†Visiting Soviet scientist under the U.S.A./U.S.S.R. Young Faculty Exchange Program. Permanent address: Department of Physics, University of Donetsk, USSR.

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Luminescence induced by ion impact on alkali-halide crystals at high temperatures (−160 to 200°C)†

A. I. Bazhin,* E. O. Rausch, and E. W. Thomas
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 12 April 1976)

A study has been made of luminescence induced by 25-keV H^+ and He^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependence of luminescence, and the effect of bleaching, in KCl and KBr. The peak intensity in the luminescent spectrum is independent of temperature from −160 to −70°C, rises to a maximum at about −10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to O_2 we also observe an additional band characteristic of O_2^-.

I. INTRODUCTION

The interaction of ionizing radiation with the solid state causes electron excitations in the form of electron-hole pairs or excitons; these subsequently decay either by a nonradiative transition with the formation of phonons and lattice defects, or by radiative transitions leading to luminescence. Intrinsic luminescence of alkali halides has been extensive investigated (see, for example, the pioneering work in Refs. 1–4); this is a fundamental luminescence associated with recombination of excited electrons with self-trapped holes (V_k centers). Intrinsic luminescence is observed for temperatures where the V_k center is stable, and for most alkali halides the radiative efficiencies and lifetimes of V_k centers begin to fall off strongly at temperatures above 100 °K due to nonradiative recombination.[4] Although efficiency of intrinsic luminescence is relatively low at temperatures of 150 °K and above, Ikeya and Crawford[5] observed a new band of luminescence in NaCl at 310 nm, which is not quenched at temperatures of 150 °K and above. They suggest that this band is associated with electron recombinations with the V_k center at some unknown impurity or by electron recombination at some type of V center formed by irradiation at room temperature. Luminescence induced by electron impact on alkali halides at 90–300 °K temperatures was extensively studied by Pinard and co-workers.[6,7] They proposed a mechanism where F centers are responsible for luminescence and quenching is related to V_3 and V_4 centers. In a study of x-ray induced luminescence at high temperatures in NaCl, Spicer[8] suggests that the luminescence centers are of the V_2- and V_4-type and emission occurs as electrons fall into these centers. Other published studies of luminescence in alkali halides at high temperatures include work on thermoluminescence,[9–11] aquoluminescence,[12,13] neutron-induced luminescence,[14] and x-ray induced luminescence in string crystals.[15,16] Previous work on luminescence induced by energetic ion impact on high-temperature crystals is restricted to the work of Alekseev *et al.*[17] concerning bombardment of KCl and NaCl by H^+; here the emission was associated with water molecules in the excited triplet state, present in the crystals as uncontrolled impurities.

In the present paper we investigate luminescence of certain alkali halides induced by the impact of H^+ and He^+ ions with energies of 5–25 keV. Targets of principal interest in this work were NaCl, NaF, KCl, and KBr; various target temperatures in the range − 160 to 200 °C were employed. The high density of electron excitation close to the target surface causes a high efficiency for defect generation in the cation sublattice and the formation of hole centers that are stable at room temperature.

II. EXPERIMENTAL PROCEDURE

The apparatus used for this work is essentially the same as that previously described for studies of light emission when ions strike metal surfaces[18]; we shall therefore give only a very brief description here. The ions are formed in an rf discharge source, accelerated and mass analyzed before being collimated and directed onto the target. Light emission from the point of beam impact on the target was viewed by a conventional scanning

monochromator observing through a sapphire window. The monochromator axis was perpendicular to the direction of the incident beam; the angle between the beam and the target surface normal could be varied but was kept at 45° for the experiments described here. The detection sensitivity of the optical system had been previously calibrated utilizing a standard tungsten filament lamp of known emissive power. The target samples were single crystals of alkali halides supplied by the Naval Research Laboratory (Washington, D. C.); they had been zone refined and had a nominal total impurity level of a few ppm or less. The samples were cleaved to a size of approximately $10 \times 6 \times 1$ mm immediately before introduction into the vacuum system. The target was mounted on a standard manipulator by Varian, providing three axes of translational motion and one axis of rotation. A specially designed target holder was employed that had a filament for heating the target region and tubes to conduct liquid nitrogen and thereby provide cooling. A number of thermocouples were provided to measure the temperature on the bombarded face of the crystal. The target chamber provided a vacuum environment with a base pressure of around 10^{-9} Torr for the work described here. After introduction into the vacuum system the targets were annealed at a temperature of 400 °C for at least 1 h in an attempt to remove surface contamination and to anneal defects in the crystal. The area of the target irradiated by the ion beam was approximately 5 mm^2 and the beam current density was generally about 10 $\mu A/cm^2$; at these current densities there was no evidence of target surface charging or electrical breakdown on the surface. Tests showed that reducing the ion beam current density by two orders of magnitude did not change the shape of the observed spectra; moreover the intensity of the spectrum was linearly proportional to beam current throughout this range. We would note that the average depth of penetration of a 25-keV H^+ ion in KCl is about 400 nm; for a 25-keV He^+ ion the depth is about 150 nm.[19] Thus, the region of excitation is very close to the surface, in contrast to studies of luminescence under x-ray and uv photon excitation where much greater penetration depths are involved.

This work was primarily concerned with the impact of H^+ and He^+ ions on alkali halides; the observed spectra were the broad bands of luminescence that we shall discuss shortly, with some line emission in the sodium-*D* when crystals containing Na were employed; this sodium emission is from sputtered atoms in excited states. Some preliminary experiments were performed with neutral hydrogen beams which gave precisely the same spectra as for H^+ and He^+ impact. We also used Ar^+ beams and observed again the same basic luminescence spectrum but with strongly enhanced emissions from sputtered alkali atoms. Spectra induced by H^+ and He^+ impact were essentially the same for new crystals and for crystals that had suffered a preliminary bombardment with Ar^+; since the argon beam will readily sputter the surface this observation suggests that surface contamination did not strongly contribute to the observed emission spectra. Some preliminary experiments were also performed using crystals supplied by the Harshaw Chemical Co. and stated to be of optical purity; the observed spectra were not significantly different from those observed with the higher-purity crystals supplied by the Naval Research Laboratory. Crystals from the latter source were employed for all the detailed measurements presented here.

Various types of data are presented here. We have recordings of the ion-induced luminescence spectra to display the relevant spectral features. We show how certain of the features vary with the temperature of the target and with the dose to which the target has been subjected. In studies of the dose dependence we measure the intensity as a function of time under continuous bombardment by a beam of constant current density. We have no knowledge of the particle density distribution in the ion beam; if inhomogeneities were present then the local dose rate might differ significantly from the dose rate integrated over the ion beam's cross sectional area. Consequently, we consider it more accurate to present data as a function of the measured parameter, time, rather than the derived parameter of dose.

III. RESULTS AND DISCUSSION

In Figs. 1 and 2 are shown spectra induced by ion beam impact on targets of KCl, KBr, NaCl, and NaF; the reader is referred to the captions for the precise conditions of bombardment in each case. The spectra are corrected for the variation of relative sensitivity with wavelength but have not been placed on an absolute scale. The spectra are typical for these samples and remain essentially unchanged in basic shape if one alters beam energy or interchanges protons and He^+ ions; such changes, however, do alter the intensity of the emission. The spectra are wide luminescent bands varying in shape between the various crystals; in addition for the NaCl crystal we observe a narrow emission line at the NaD wavelength corresponding to atomic line emission from sputtered sodium atoms. In our following discussions we shall concentrate principally on the KCl and KBr spectra and con-

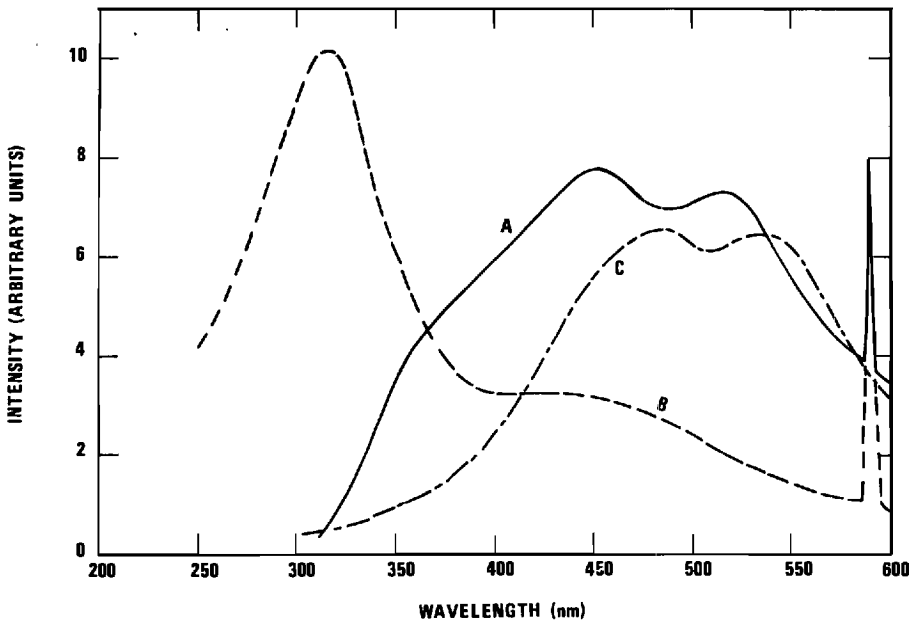

FIG. 1. Luminescence spectra of certain alkali halides at room temperature under bombardment by 25-keV projectiles. A, NaCl bombarded by a 10-μA/cm^2 H^+ beam at a temperature of 20 °C; B, NaF bombardment by a 6-μA/cm^2 He^+ beam at a temperature of 22 °C; C, KBr bombarded at a 10-μA/cm^2 H^+ beam at a temperature of 22 °C.

sider in detail the effects of annealing, temperature variation, and dose.

An initial test was made to determine whether any of the band spectrum was linked to impurities. We recorded the ion-induced luminescence spectrum from KCl and KBr crystals both in their freshly cleaved state before annealing and also after annealing for 5 h at 450 °C in the 10^{-9}-Torr vacuum environment. We found that annealing caused a substantial reduction of intensity at wavelengths around 530 nm, suggesting a band at this point associated with impurities. To confirm this we exposed annealed samples to nitrogen and oxygen gas for 5 min or more at a pressure of 10^{-6} Torr. Nitrogen caused no change to the spectrum but oxygen caused a rise of intensity at 530 nm by a factor of 3 and restored the spectrum to the form observed before annealing. Figure 3 shows a spectrum of KBr after oxygen absorption which should be compared with the typical spectrum of an annealed sample shown as Fig. 1(C). The annealed sample shows a small residual peak at 530

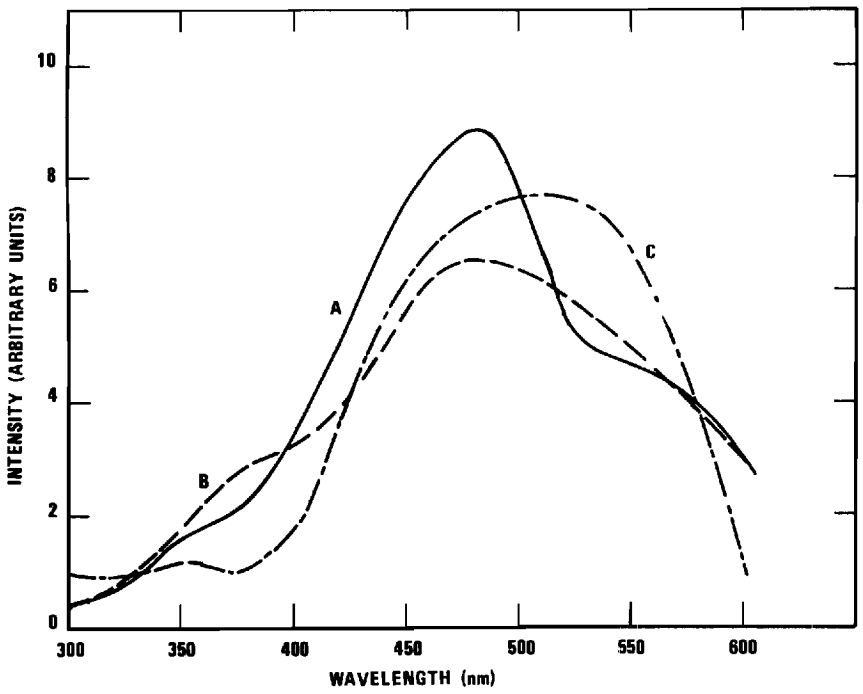

FIG. 2. Luminescence spectra of KCl and KBr at low temperature under bombardment by a 10-μA/cm^2 beam of 25-keV H^+ ions. A, KCl at −29 °C; B, KCl at −50 °C; C, KBr at −150 °C.

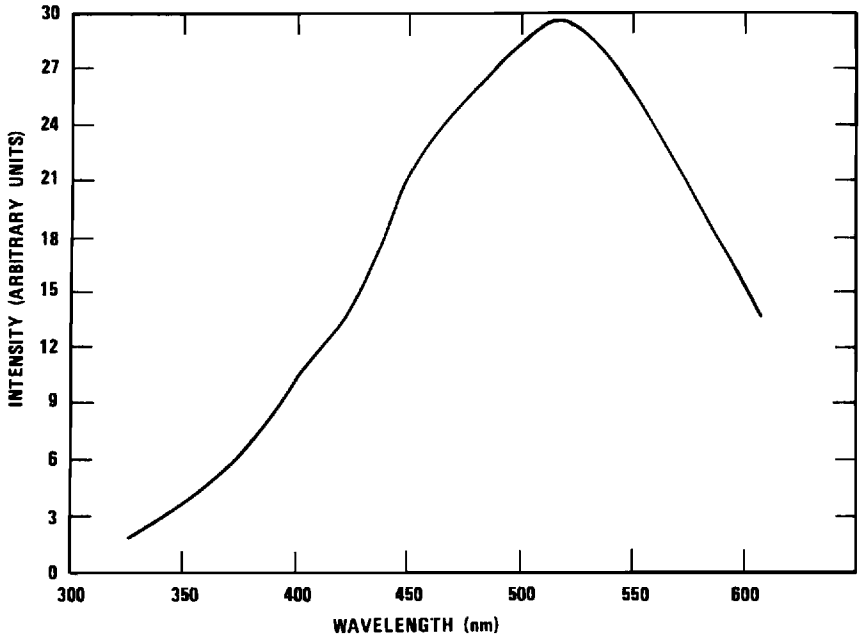

FIG. 3. Luminescence spectrum of KBr after absorption of O_2 at 10^{-6} Torr; projectile beam is 25-keV He^+ at a current density of 6 $\mu A/cm^2$ and target temperature is 29°C.

nm but the sample with oxygen exposure is dominated by the 530-nm peak which covers and obscures the peak at 480 nm. Similar results are found with KCl and NaCl samples. We believe that the 530-nm band is due to oxygen impurities on the surface. Rolfe *et al.*[20] have studied the fluorescence of NaCl, KCl, and KBr doped with O_2^- and find a band which peaks at 530 to 550 nm, depending on the crystal; we do not, however, observe the vibrational structure seen when O_2^- is a substitutional impurity.[20] In the work that follows all crystals were first annealed to a temperature of 400 °C for 1 h or more to reduce or remove the influence of the oxygen contamination.

The most significant features of the room-temperature spectra of KCl and KBr are peaks at 480 and 500 nm, respectively; we shall later show that these are due to recombination of electrons from the conduction band with V_3 centers. At low temperatures (Fig. 2) we also observe for these same targets a weak peak at lower wavelengths, 370 nm for KCl and 350 nm for KBr; we shall later show that these peaks are due to recombination of conduction band electrons with V_4 centers. The low-wavelength peaks are strongly overlapped by the more-intense high-wavelength peak and show up on the spectra as only weak shoulders; they are, however quite reproducible.

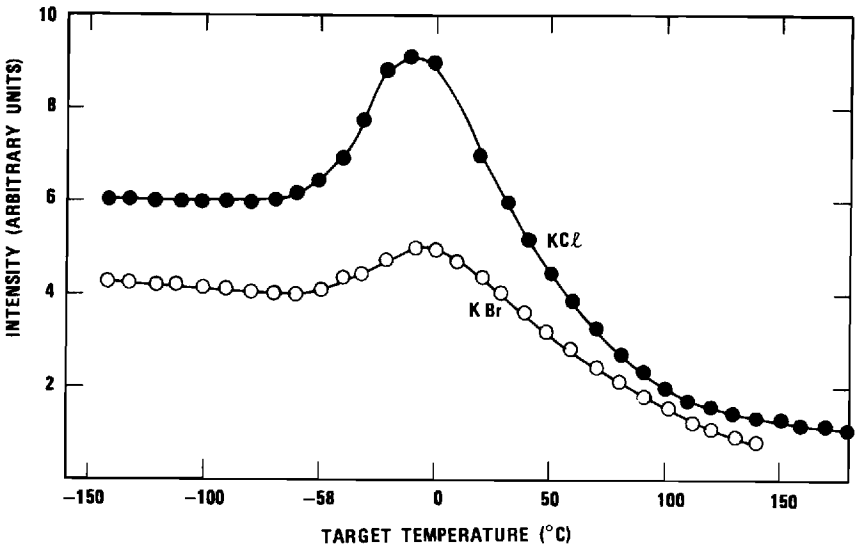

FIG. 4. Dependence of the luminescence intensity on target temperature. Targets are KCl and KBr; bombarding beam is 25-keV H^+ at a density of 10 $\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

In Fig. 4 we show measurements of luminescent intensity as a function of temperature for KCl and KBr crystals. The intensity is measured at 480 nm for KCl and 500 nm for KBr with a spectral resolution of 4.8 nm; these wavelengths correspond to the peaks of intensity in these spectra. It was found that the ion beam impacting on a crystal at low temperatures could cause a significant temperature rise. Consequently, the ion beam was pulsed on for only 2 sec at each temperature in order that temperature rise should be kept less than 1 °C. Figure 4 shows that luminescent intensity is constant as temperature rises from – 150 to about – 50 °C then rises to a weak maximum at about – 10 °C and decreases for further increase in temperature. Provided the crystal had been properly annealed before commencing the measurement we found no difference between data taken as temperature increased and data taken with decreasing temperatures.

If the luminescence centers are lattice defects arising during ion bombardment, then a study of intensity as a function of dose should represent the formation of the relevant radiation defects. To study such behavior an annealed crystal was bombarded continuously for a period of 10–20 min using a H^+ beam of 10-μA/cm^2 flux density. A continuous record of intensity as a function of time, and therefore dose, was performed. Figures 5 and 6 show the results for KBr and KCl crystals at room temperature and at a lower temperature. Low-temperature behavior (Fig. 5) shows three distinct regions. First a rapid decrease of intensity over a period of 1 min; secondly a rising intensity extending over a bombardment time of 3–8 min, depending on the sample; finally the third region is a very slow decline of intensity which appears to continue indefinitely. By contrast the room-temperature behavior (Fig. 6) is an initial rapid rise, followed by a rapid fall and finally at bombardment time of 8 min or more a slow decline that continues indefinitely.

In the studies of dose dependence (Figs. 5 and 6) there are regions where intensity increases as a function of dose; these suggest that the centers responsible for luminescence are created by ion bombardment. However, the intensity of luminescence is not zero at the commencement of bombardment so that some luminescent centers are already present in the unbombarded crystal despite the preliminary annealing procedure. The fact that intensity is a function of temperature shows that the formation, and the stability, of the defects responsible for luminescence is temperature dependent. It is known that during irradiation of KBr and KCl at temperatures close to room temperature one forms[21] stable electron centers of the F and F_2 (M) types and also hole defects of the V_3 type (this center being designated V_x by Lushchik *et al.*[16]). In order to try to separate the roles of these different centers we performed some simple light bleaching experiments. First the crystals were bombarded with H^+ ions for a time of 10 min or more so that the luminescence intensity corresponded to a point on Fig. 6 in the final section of the dose dependence where intensity decreases slowly as dose is increased. Then, with the ion beam removed, the crystal was exposed to light in the F-band absorption region provided by a tungsten filament lamp and suitable ab-

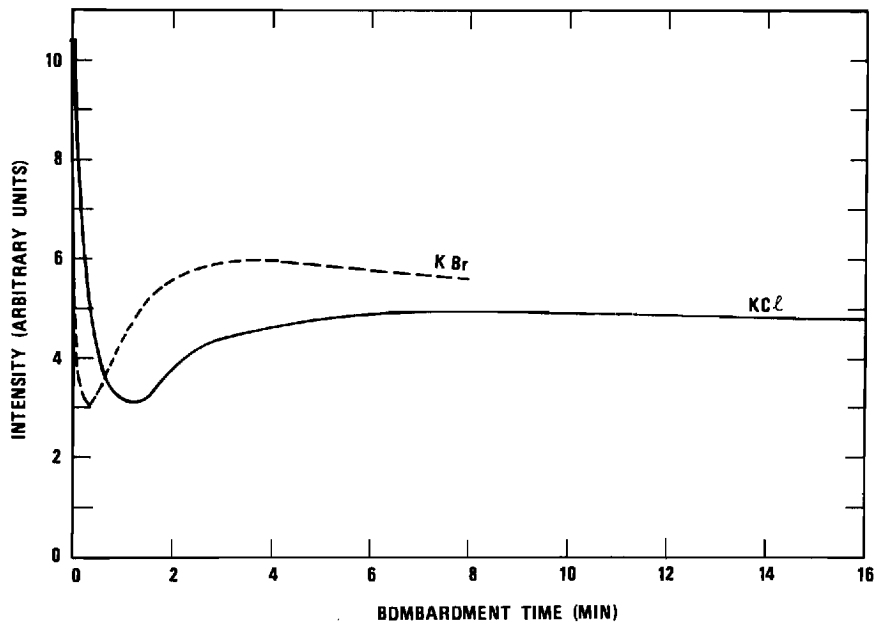

FIG. 5. Dependence of luminescence intensity on dose for targets at low temperature. Targets are KCl at – 135 °C and KBr at – 150 °C; bombarding beam is 25-keV H^+ at a density of 10 μA/cm^2. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

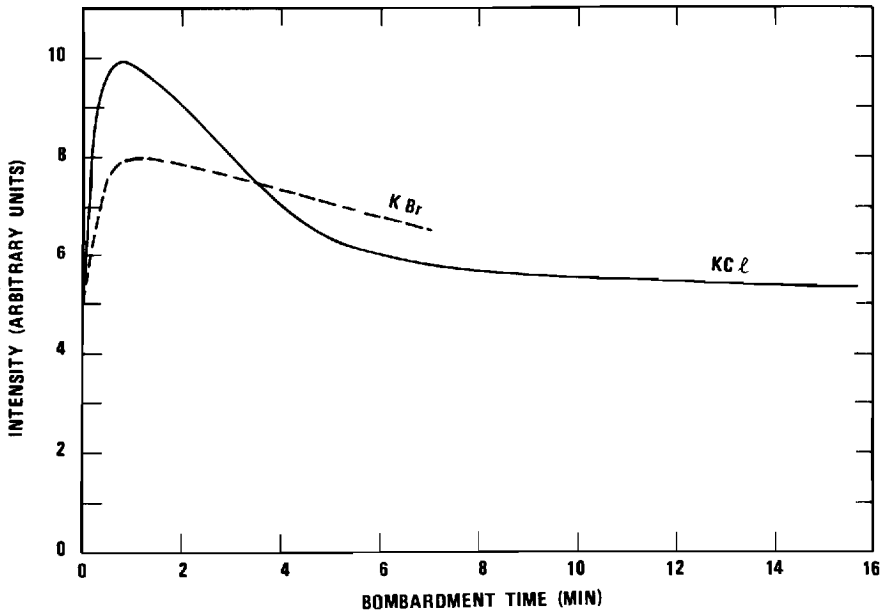

FIG. 6. Dependence of luminescence intensity on dose for targets at room temperature (22 °C). Targets are KCl and KBr; bombarding beam is 25-keV H^+ at a density of 10 μA/cm^2. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

sorption filters; we used 560 nm for KCl and 620 nm for KBr with a bandwidth of 140 nm in both cases. The bleaching was terminated after 30 min and ion bombardment recommenced. The intensity of the ion-induced luminescence was unchanged by the attempt of F-center bleaching. We also exposed the crystal to unfiltered white light which should bleach more complicated electron centers; again no effect was observed. Thus no effect of bleaching was found and we conclude that the centers of luminescence can be V_3 centers which are known[21] not to be bleached by white light.

We propose that the V_3 center is responsible for the principal luminescent intensity at 480 nm in KCl [Figs. 1(C) and 2(C)] and 500 nm in KBr [Figs. 2(A) and 2(B)]; it is known[21,22] that the V_3 center is stable up to 200 °C. At low temperatures we also observe a small peak at 370 nm in KCl and 350 nm in KBr [see Figs. 2(B) and 2(C)]; we propose that the V_4 center is responsible for this feature. The low-wavelength peak does not appear to be connected with impurities and as temperature is raised the feature is no longer apparent. It is known[23] that at temperatures below – 30 °C the V_4 center occurs in addition to the V_3 center. However, at all temperatures considered here the luminescence we identify as due to V_3 centers, predominates. In Fig. 7 are shown the structures postulated for the V_3 and V_4 centers.[16,22] The X_3^- molecule occupies a divacancy to form a V_4 centers, and the X_3^- molecule occupies one cation and two anion vacancies to form the V_3 center. If, as we suggest, the V_3 and V_4 centers are responsible for these emission bands then the sum of energy of emitted photon and the energy of V_3- and V_4-center photon absorption, should equal the band-to-band energy. In Fig. 7 we show an energy level scheme appropriate to KCl with the suggested radiative recombination transition. In Table I we list the band-gap energies for KCl, KBr, and NaCl with the energy of photon emission which we identify as due to recombination of electrons with the V_3 and V_4 centers; also listed are the photon energies of maximum absorption ascribed by others[26,28] as due to the V_3 and V_4 centers. In KCl the band gap is quoted[24] as 8.5 eV and the energies for photoabsorption by V_3 and V_4 centers are 5.85 and 5.16 eV, respectively[26,28]; thus the predicted energies of photon emission in recombination of

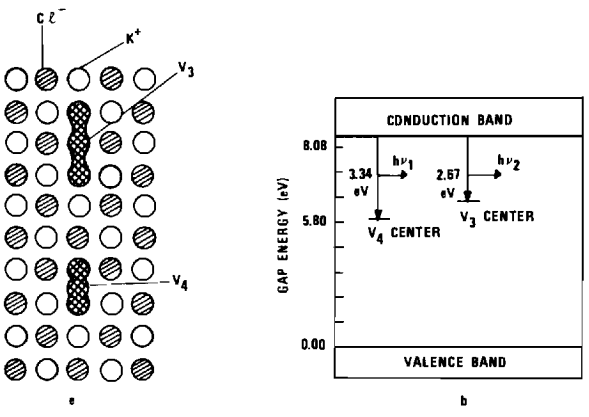

FIG. 7. Diagram of the structure ascribed to V_3 and V_4 centers with an energy level diagram for KCl showing the position of the energy levels associated with such centers.

TABLE I. Known band-gap energies and known photon energies for absorption maxima in the V_3 and V_4 bands presented with the photon energies (and wavelengths) of the peak intensity observed in the present luminescence studies. Band I is the high-wavelength band we ascribe to the V_3 center and band II is the low-wavelength band we ascribe to the V_4 center.

Sample	Energy gap (eV)	Absorption-band maxima (eV) V_3	V_4	Observed luminescent band maxima Band I Energy (eV)	Band I Wavelength (nm)	Band II Energy (eV)	Band II Wavelength (nm)
NaCl	8.6 [a]	5.9 [b]	5.56 [c]	2.76	450	3.31	375
KBr	7.8 [a]	5.35 [c]	4.5 [d]	2.48	500	3.54	350
KCl	8.5 [a]	5.85 [c]	5.16 [e]	2.58	480	3.35	370

[a] Reference 24.
[b] Reference 25.
[c] Reference 26.
[d] Reference 27.
[e] Reference 28.

electrons with V_3 and V_4 centers are 2.65 and 3.34 eV, respectively. Hence we expect emission at 468 nm for the V_3 center and 371 nm for the V_4 center; quite close to our observed peaks at 480 and 370 nm. This reinforces our conclusion that the observed luminescence is due predominantly to recombination of electrons with V_3 centers and that at low temperatures there is an additional small feature caused by recombination of electrons with V_4 centers.

It is difficult to make precise statements about the width of our observed luminescence bands since there is considerable overlap between the prominent V_3 band, the weak V_4 band and residual effects of the O_2^- impurity band. However, a rough estimate of the V_3 bandwidth at half-maximum for KCl [Fig. 2(A)] is 1.1 eV; this is consistent with the width of the V_3 absorption band which is about 1.2 eV in the measurements of Seretlo.[21]

With the identification of the emission as being due to electron recombination with V_3 and V_4 centers we should now be in a position to understand the dependence of intensity on temperature and irradiation dose. The intensity of the ion-induced luminescence will undoubtedly depend on the rate of electron excitation to the conduction band and on nonradiative decays of such electrons; also intensity will depend on the density of relevant recombination centers through their rates of creation and rates of annealing. Thus the relationship of luminescent intensity to dose and temperature is more complex than the relationship of directly measured V_3- and V_4-center density to these same experimental parameters. It would be presumptuous, and possibly misleading, to attempt a modeling of the phenomenon based only on the measured parameter of intensity; supporting information on the directly measured defect-center concentrations would be necessary in order to develop a reliable quantitative understanding. Nevertheless a general qualitative explanation may be achieved by studying the close correlations between the present work and previously published direct measurement of F-, V_3-, and V_4-center densities induced by x-ray, electron, and ion irradiation. We should note that V_3- and V_4-type centers are complementary to the F center and should therefore exhibit the same rate of formation with dose. The ion fluxes used in these studies (10 $\mu A/cm^2$) represent a rather high dose rate compared with previous studies of defect-center concentration induced by x-ray irradiation. In the work of Alekseev[17] on bombardment of NaCl by 30-keV H^+ it was found that the F-center concentration saturated at 5.35×10^{18} cm^{-3}. By comparison the studies of F-center formation under x-ray irradiation by Seretlo[21] involved a maximum F-center density of 1.5×10^{17} cm^{-3} in the irradiated sample; most irradiations were smaller.

Hughes and Pooley[29] have studied F center growth in KCl under bombardment by protons of 100-keV energy and above at high doses. F-center concentration increases to a saturation and then decreases with further increase of dose. This behavior is explained in terms of a spontaneous recombination (athermal annealing) of interstitials and vacancies. Two competing mechanisms are involved.[29] In the first, one argues that an interstitial (or vacancy) formed within some critical distance of a vacancy (or interstitial) will recombine so that no new defect center is produced. The second mechanism is a "back reaction" where F centers diffuse and either recombine with interstitials they encounter or else form F center aggregates. These mechanisms together can predict a rise in F center (and hence V_3 and V_4 center) concentration, followed by saturation, and a subsequent decrease. We observe such behavior

for luminescence in room-temperature irradiation (Fig. 6) and for most of the low-temperature irradiation (Fig. 5); thus emission intensity mirrors the expected behavior of V_3- and V_4-center density. We note that Hughes and Pooley[29] find F-center concentration to saturate at a dose of about 10^{19} ions/m^2 for 100-keV impact at room temperature. In comparison, our data for 25-keV H^+ impact show saturation at a dose of about 4×10^{19} ions/m^2 at room temperature and 2×10^{20} ions/m^2 at $-150\,^\circ$C; thus our doses for saturation of luminescence are quite comparable with the previously observed[29] dose for saturation of F-center concentration. We can provide no explanation of the low-dose behavior in Fig. 5 where an initial rapid decrease of intensity is observed. However we note that similar behavior is seen in cathodoluminescence studies by Nouailhat *et al.*,[7] and in conductivity studies of string crystals by Melik-Gaikazyan *et al.*[15] This behavior has been ascribed[15] to the destruction of preirradiation defects.

Neglecting the effects of nonradiative electron transitions, the luminescence intensity as a function of temperature (Fig. 4) should mirror the V_3-center concentration. Seretlo[21] has studied thermal annealing of V_3 centers that were created by x-ray irradiation. For the highest irradiation densities utilized, Seretlo observes the V_3-center concentration to decrease generally monotonically with temperature above 30 °C, with the exception of a small unexplained peak at 70 °C. Our data on luminescence intensity of the V_3 band as a function of temperature above 0 °C show essentially the same behavior, apart from the unexplained peak. At temperatures below $-20\,^\circ$C our intensity in the V_3 band decreases and becomes constant. In this temperature region we observe increasing prominence of the low-wavelength emission band ascribed to recombination on V_4 centers; the V_4 center is, of course, an alternative final state for displaced atoms. We conjecture that the sum of V_3- and V_4-center concentrations may remain relatively constant at low temperatures but that the V_4 centers assume greater importance than at room temperatures and the V_3-center luminescence therefore decreases.

IV. CONCLUSION

The luminescence induced by impact of 25-keV H^+ and He^+ ions on KCl and KBr consists of an intense broad band peaking at around 500 nm. We identify this band as due to electron recombination with V_3 centers. At low temperatures there is a second weak feature around 360 nm which we identify as due to electron recombination with V_4 centers. The photon energies at the emission intensity peak are consistent with the known band gap and known energies of the V_3 and V_4 centers established by photoabsorption measurements. The behavior of the luminescence intensity as a function of temperature and dose is quite consistent with other more direct measurements of F-, V_3-, and V_4-center formation.

ACKNOWLEDGMENTS

We are indebted to Dr. Howard Lessof of the Naval Research Laboratory, Washington, D. C. for the supply of many of the samples used in this work. Also we acknowledge the assistance of Dr. M. Zivitz in the early states of this work. One of us (A. I. B.) acknowledges support from the International Research and Exchanges Board.

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†Supported in part by a grant from the Division of Materials Research of the NSF.

*Visiting Soviet Scientist under the "U.S.A/U.S.S.R. Young Faculty Exchange Program." Permanent address: Dept. of Physics, University of Donetsk, Donetsk, USSR.

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

OFFICE OF
THE DIRECTOR OF
FINANCIAL AFFAIRS

December 13, 1977

Division of Grants and Contracts
National Science Foundation
Washington, D. C. 20550

Gentlemen:

Enclosed in triplicate is the final fiscal report for Grant Number DMR-73-2317 formerly GH-40217.

If you have any questions or desire additional information, please let us know.

Sincerely yours,

Evan Crosby

Evan Crosby
Associate Director of
Financial Affairs

EC/bs
cc: Dr. E. W. Thomas
Dr. J. R. Stevenson
Mr. E. E. Renfro
Mr. A. H. Becker
File G-41-325

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

RESEARCH GRANT BUDGET & FISCAL REPORT

Form Approved
OMB No. 99-R0013

INSTITUTION AND ADDRESS	NSF PROGRAM	GRANT PERIOD
Georgia Inst. of Technology Atlanta, Georgia	Solid State Physics	*from* 10/1/73 *to* 9/30/77
		REPORTING PERIOD *from* 10/1/73 *to* 11/23/77*
GRANT NUMBER: DMR73-02317 A02	BUDGET DUR. (MOS.): 12	PRINCIPAL INVESTIGATOR(S): Thomas
		GRANTEE ACCOUNT NUMBER: G-41-630

	NSF Funded Man Months Cal.	Acad.	Summ.	NSF AWARD BUDGET	CUMULATIVE GRANT EXPENDITURES *Do Not Round*
A. SALARIES AND WAGES					
1. Senior Personnel					
a. 1 (Co)Principal Investigator(s)			2	$ 4,239	
b. Faculty Associates					
Sub-Total				$ 4,239	$ 9,219.00
2. Other Personnel (Non-Faculty)					
a. Research Associates—Postdoctoral					
b. Non-Faculty Professionals					
c. 2 Graduate Students				7,500	
d. ~~Pre-Baccalaureate~~ Students					
e. Secretarial—Clerical					
f. 1 Technical, Shop, and Other				200	
TOTAL SALARIES AND WAGES				$ 11,939	$ 30,195.27
B. STAFF BENEFITS IF CHARGED AS DIRECT COST				397	916.71
C. TOTAL SALARIES, WAGES, AND STAFF BENEFITS (A + B)				$ 12,336	$ 31,111.98
D. PERMANENT EQUIPMENT					8,561.59
E. EXPENDABLE EQUIPMENT AND SUPPLIES				4,000	11,841.29
F. TRAVEL 1. DOMESTIC (INCLUDING CANADA)				500	1,935.45
2. FOREIGN					765.01
G. PUBLICATION COSTS					1,581.00
H. COMPUTER COSTS IF CHARGED AS DIRECT COST					
I. OTHER DIRECT COSTS					
J. TOTAL DIRECT COSTS (C through I)				$ 16,836	$ 55,796.32
K. INDIRECT COSTS 65% of $10,970.71 = $ 7,130.97 68% of Salaries and Wages 68% of 19,224.56 = 13,072.71				8,118	20,203.68
L. TOTAL COSTS (J plus K) $30,195.27 $ 20,203.68				$ 24,954	$ 76,000.00
Less Residual Funds				1,800	
M. AMOUNT OF THIS AWARD (ROUNDED)				$ 23,200	
N. CUMULATIVE GRANT AMOUNT				$ 76,000	
O. UNEXPENDED BALANCE (N. BUDGET MINUS L. EXPENDITURE)					$ -0-

REMARKS: Use extra sheet if necessary

*No obligations were incurred outside the grant period of 10/1/73 through 9/30/77.

SIGNATURE OF PRINCIPAL INVESTIGATOR	TYPED OR PRINTED NAME	DATE
E. W. Thomas	E. W. Thomas	8 Dec 1977

I CERTIFY THAT ALL EXPENDITURES REPORTED ARE FOR APPROPRIATE PURPOSES AND IN ACCORDANCE WITH THE AGREEMENTS SET FORTH IN THE APPLICATION AND AWARD DOCUMENTS

SIGNATURE OF AUTHORIZED OFFICIAL	TYPED OR PRINTED NAME & TITLE	DATE
Evan Crosby	Evan Crosby, Associate Director of Financial Affairs	12/13/77

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Organ. Code	F.Y.	Fund ID	Prog. Code	Ob. Class	O/Dres.	Award No.	Amd.	Inst. Code	Unexpended Balance	Trans.	Lot
									$		

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G-41-630

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SCHOOL OF PHYSICS

October 7, 1977

Dr. Dean Mitchell
Program Director
Solid State Physics Program
Condensed Matter Sciences Section
National Science Foundation
Washington, D. C. 20550

Dear Dr. Mitchell,

By this letter I convey to you the "Final report" to project DMR 73-02317 A02 as stipulated in NSF publication NSF-73-12. The report is very abbreviated since all the results from this work have been published. Copies of all journal publications have been sent to you earlier; two other items (a conference paper this summer and a book chapter) will be sent when they are available.

I regard this as one of the most successful projects I have undertaken. I am very grateful for the support provided by NSF and the interest shown by yourself and your predecessors Drs. Silberglitt and Budnick.

Yours sincerely,

E. W. Thomas

E. W. Thomas
Professor

Enc. 1. Final Technical Report
2. Form 98A

EWT/ar

Collision Induced Optical Spectra of Solids

Final Technical Report

by

E. W. Thomas

NSF Grant DMR 73-02317 A02

School of Physics

Georgia Institute of Technology

Atlanta, Georgia 30332

Index

I. Name of Institution: Georgia Institute of Technology

II. Name of Principal Investigator: Edward W. Thomas, Professor of Physics.

III. Grant No.: DMR 73-02317 A02

IV. Starting Date: 10/1/73

V. Completion Date: 9/30/77

VI. Title: Ion Induced Optical Spectra of Solids

VII. Research and Results:

The purpose of this project was to study emission spectra of solids induced by the impact of energetic (5 to 200 keV) ions. The original proposal was prompted by our preliminary observations of continuous or broad band emission when certain metals and insulators were bombarded. These continua emanate from the solid and represent transitions between bands; electron-hole or electron-defect recombination mechanisms can be responsible. During the course of our studies we discovered also broad band emission from particles ejected from the surface; this appears to be restricted to the transition metals and involves very long lived states that travel up to one centimeter from the surface before emitting. We have shown that these continua from transition metals occur only when contaminant oxygen is present and that the ejected species is a metastable Mo O^* molecule. In studies of luminescence from alkali halides we have discovered a vibrational molecular spectrum; this has been identified as due to CN radicles formed by some ion induced chemical reaction of surface contaminants. The observed spectra lines have considerable intristic breadth due to the interaction of the CN radicle with the surface.

The research program commenced originally with a study of intristic luminescence; this phenomenon may be properly termed "ionoluminescence". Unexpectedly this lead to the identification of ejected transition metal oxides;

conventional spectroscopic sources provide no information on these species since the ground state (e.g. of Mo O) is apparently repulsive over large ranges of internuclear separation. Finally the project lead also to the first identification of an ion induced chemical reaction.

An significant information generated by this project has now been published in the open literature. Consequently it is appropriate to report the scientific results by reproducing the abstracts of the more important publications.

A. Intristic Luminescence of Metals

The first study under this grant was of the intristic luminescence of certain metals. We concentrated particularly on the emission from Al induced by 10 to 30 keV H^+ and He^+ ; we predicted the spectrum theoretically on the basis of electron-hole recombination. The results have been reported: M. Zivitz and E. W. Thomas, Phys. Rev. B., 13, 2747 (1976) and the abstract is as follows:

> Impact of 10- to 30-keV H^+ and He^+ ions on polycrystalline Al, Cu, and Mo targets induces broad-band light emissions in the photon energy range of 2-6 eV; these emissions emanate from the target. For aluminum the emission is particularly intense, increases linearly with incident beam current, and is invariant in relative shape with projectile energy and angle of incidence. The dominant peak is at a photon energy of 2.4 eV; and a weak shoulder is observed at 3.3 eV. An electron-hole recombination model is shown to account for the general form of the emission band. We also calculate the electron density of states and the complex part of the dielectric constant ε_2; the energy-band structure based on Ashcroft's Al pseudopotential is presented in tabular form.

B. Ion Induced Luminescence of Alkali Halides

We have studied extensively the broad band emissions resulting from light ion (H^+ and He^+) impact on alkali halides (LiF, NaCℓ, NaF, KBr, KF). The results have been reported: A. I. Bazhin, E. O. Rausch and E. W. Thomas, Phys. Rev. B, 14, 2583, (1976). The abstract is as follows:

A study has been made of luminescence induced by 25-keV H^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependence of luminescence, and the effect of bleaching, in KCℓ and KBr. The peak intensity in the luminescent spectrum is independent of temperature from - 160 to -70°C, rises to a maximum at about 10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to $^3O_2$ we also observe an additional band characteristic of O_2^-.

C. The Broad Band Optical Emission from Mo, Nb, and W Bombarded by Heavy Ions

The most puzzling aspect of ion-induced emission from solids has been the continuum emission induced by impact of heavy ions (Ne^+, Ar^+ etc.) on certain metals; the transition metals all show the phenomenon and Mo has been the case most frequently studied. These spectra were reported by at least three groups but no definite explantaion of its origin was provided. We have shown quite conclusively that the spectrum occurs only in the presence of oxygen. A paper on this phenomenon has been published: E. O. Rausch, A. I. Bazhin, and E. W. Thomas, J. Chem. Phys. 65, 4447 (1976). The abstract is as follows:

Continuum emission has been observed when Mo, W and Nb targets were bombarded with 10 to 30 keV, Ne^+, and Ar^+. The emission occurs only when the environment of the target chamber contains an oxygen partial pressure of 2×10^{-9} torr or above; for lower pressures the emission is absent. Identical continua are also observed when the metal oxides are bombarded with Ne^+ and Ar^+; similar spectral features, though with changed relative intensities, are seen when the targets are bombarded with O^+ and O_2^+ ions in the absence of O_2 gas in the vacuum environment. A significant feature of these continua is that the emitting species extend for some mm beyond the bombarded surface. we suggest that the source of the emission is sputtered oxides of the target. The variation of emission intensity with oxygen partial pressure and bonbarding ion beam current is consistent with a mechanism where the oxide is formed by the simultaneous sputtering of an absorbed oxygen atom and a metal atom from the bulk material.

D. Ion Induced Luminescence of CN Molecules on Alkali Halide Surfaces

Impact of light ions on alkali halides produces a distinct band spectrum in the wavelength region 230-350 nm; which has the features of a vibrational structure of an electronic transition in a molecule; the source of the emission is located at the surface. We have concluded quite definitely that the emission is from CN radicals on the surface, whose origin lies in adsorbed contaminants. A paper on this phenomenon is published. A. I. Bazhin, E. O. Rausch and E. W. Thomas, J. Chem. Phys. 65, 3897 (1976). The abstract follows:

> During a study of luminescence induced by low energy (20 keV) light ion (H^+, He^+) impact on certain alkali halides (LiCℓ, NaBr, NaCℓ, KBr, KCℓ) we have observed a band spectrum in the region 230 nm to 350 nm. The bands are separated by 0.26 eV and have a half width of 0.12 eV; no fine structure is observed. Identical bands of much increased intensity are observed when samples deliberately doped with CN are bonbarded. The phenomenon is not found with KBr crystals. We suggest that the observed bands are due to transition in the CN molecules, the $D^2\Pi_1 - X^2\Sigma^+$ transition that is observed as a very weak transition in discharges. The mechanism whereby CN is formed on the samples remains unclear but appears to be influenced by the presence of adsorbed water.

E. General Conclusion

The original objective of the project was to understand the continuum or broad band luminescence of certain metals and alkali halides; this was accomplished quite readily. In the course of the work we successfully explained for the first time the continuum emission observed outside transition metal surfaces. Also we detected the formation of CN on alkali halides; probably the first published example of an ion induced surface chemical reaction.

VIII. Publications

1. "Ionoluminescence of Aℓ, Cu, and Mo; Optical Properties of Aluminum" M. Zivitz and E. W. Thomas. Phys. Rev. B 13, 2747 (1976).

2. "Ionoluminescence of Aluminum". M. Zivitz and E. W. Thomas. Proceedings of the 6th International Conference on Atomic Collisions in Solids, Amsterdam, Sept. 1975. Nucl. Inst. and Meth., 132, 411 (1976).

3. "Luminescence Induced by Ion Impact on Alkali Halide Crystals at High Temperatures (-160°C to 200°C). A. I. Bazhin, E. O. Rausch and E. W. Thomas. Phys. Rev. B 14, 2583 (1976).

4. "Ion Induced Luminescence of Alkali Halides with CN Impurity", A. I. Bazhin, E. O. Rausch, and E. W. Thomas. J. Chem. Phys. 65, 3897 (1976).

5. "On the Origin of Broad Band Optical Emission from Mo, Nb, and W Bombarded by Heavy Ions," E. O. Rausch, A. I. Bazhin and E. W. Thomas. J. Chem. Phys. 65, 4447 (1976).

6. Ion Induced Photon Emission From Solids. E. W. Thomas. "Proceedings of the 7th International Conference on Atomic Collisions in Solids." (Moscow University Publishing House, Moscow 1977).

7. "Optical Emission from Low Energy Ion Surface Collisions." Chapter in "Inelastic Ion Atom Collisions" (Academic Press, N.Y. 1977, N. H. Tolk, Editor).

IX. Invited Papers at Conferences

1. "Optical Emission from Low Energy Ion Surface Collisions". Invited paper at the International Workshop on Inelastic Ion Surface Collisions; Murray Hill, N. J. July 1976.

2. "Ionoluminescence" Invited Paper, Gordon Conference on Particle Solid Interactions, Proctor Academy, N.H. July 1976.

3. "Formation of Excited States by Ion Impact on Surfaces", Invited Paper, APS meeting in San Diego, March 21, 1977. Pulbished in Bull. Am. Phys. Soc. 22, 273 (1977).

4. "Ion Induced Photon Emission from Solids." Invited Paper. 7th International Conference on Atomic Collisions in Solids, Moscow, 19th September 1977.

X. Other Seminars and Contributed Papers

1. "Light Emission Induced by Ion Impact on a Surface". Contributed Paper, Fifth Annual Meeting of the Division of Electron and Atomic Physics of the American Physical Society, New Haven, Conn., December 1973. Published in Bull. Am. Phys. Soc. 18, 1504 1973.

2. "Quantum Tunneling at Surfaces" Seminar, University of South Carolina, Columbia, S. C. April 25, 1974.

3. "Excitation Induced by Ion Impact on Surfaces", Seminar, Auburn University Auburn, Alabama, November 3, 1973.

4. "Luminescence of Alkali Halides due to Ion Impact". Contributed Paper, Fall meeting of the American Physical Society, Atlanta, Ga., Dec. 4, 1974. Published in Bull. Am. Phys. Soc. 19, 1081 (1974).

5. "Ionoluminescence of Aluminum". Contributed Paper; VIth International Conference on Atomic Collisions in Solids, Amsterdam, September 1975.

6. "Light Emission Induced by Ion Impact on Surfaces". Seminar, Sandia Laboratories, 2 Dec. 1975.

7. "Luminescence of Alkali Halide Monocrystals Induced by Ion Beam Excitation", March Meeting of the APS, Atlanta, Georgia, April 1, 1976. Published in Bull. Am. Phys. Soc. 21, 438 (1976).

8. "Optical Emission from Ion-Bombarded Surfaces" Lecture U. K. Atomic Energy Authority, Harwell, England, 2 September 1977.

XI. Theses

1. Optical Investigation of Ion-Metal Collisions. Ph.D. thesis by W. E. Baird; Georgia Institute of Technology.

XII. Inventions or Discoveries

We claim no patentable inventions. However there are two major discoveries that should be recognised.

1. A method for producing, by sputtering, long lived excited transition metal oxides which produce continuum emission. This is the first effective mechanism for producing spectra of transition metal oxides; since there is an inherent population inversion there is some potential for use as a tuneable laser mechanism.

2. Discovery of the process of ion induced (or catalyzed) chemical reactions on a surface leading to formation of cyanide.

XIII. Scientific Collaborators

The following have collaborated in this NSF funded project although in some cases no direct financial support of income was provided .

1. Maury Zivitz. Post Doctoral Assistant.

2. E. O. Rausch. Post Doctoral Assistant.

3. Anatoli I. Bazhin. Faculty member of Donetsk University in the USSR. Visting faculty member at Georgia Tech. under the USA-USSR young faculty exchange program.

4. W. E. Baird. Ph.D. student.

5. M. Murray. M. S. student.

6. H. Inouye. M. S. student with fellowship from Sony Corp. of Japan.

7. W. Metz. Ph.D. student.

XIV. Comments

The principal investigator has secured funding under NSF grant DMR77-04110 (effective 8/1/77) for further work on certain aspects of this program. Specifically the grant will cover a study of the chemical reaction which leads to CN formation (see VII. D) and similar reactions leading to CH formation.

XV. Signature

E. W. Thomas

E. W. Thomas
Professor
Principal Investigator

10/4/77

Date

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

SUMMARY OF COMPLETED PROJECT

Form Approved
OMB No. 99R0013

Please read instructions on reverse carefully before completing this form.

1. INSTITUTION AND ADDRESS	2. NSF PROGRAM	3. GRANT PERIOD
School of Physics Georgia Institute of Technology Atlanta, Georgia 30332	Division of Materials Research	from 10/1/73 to 9/30/77

4. GRANT NUMBER	5. BUDGET DUR. (MOS)	6. PRINCIPAL INVESTIGATOR(S)	7. GRANTEE ACCOUNT NUMBER
DMR 73 02317	48	E. W. Thomas	G-41-630

8. SUMMARY (Attach list of publications to form)

The purpose of this project was to study emission spectra of solids induced by the impact of energetic (5 to 200 keV) ions. The original proposal was prompted by our preliminary observations of continuous or broad band emission when certain metals and insulators were bombarded. These continua emanuate from the solid and represent transitions between bands; electron-hole or electron-defect recombination mechanisms can be responsible. During the course of our studies we discovered also broad band emission from particles ejected from the surface; this appears to be restricted to the transition metals and involves very long lived states that travel up to one centimeter from the surface before emitting. We have shown that these continua from transition metals occur only when contaminant oxygen is present and that the ejected species is a metastable Mo O* molecule. In studies of luminescence from alkali halides we have discovered a vibrational molecular spectrum; this has been identified as due to CN radicles formed by some ion induced chemical reaction of surface contaminants. The observed spectra lines have considerable intristic breadth due to the interaction of the CN radicle with the surface.

The research program commenced originally with a study of intristic luminescence; this phenomenon may be properly termed "ionoluminescence". Unexpectedly this lead to the identification of ejected transition metal oxides; conventional spectroscopic sources provide no information on these species since the ground state (e.g. of Mo 0) is apparently repulsive over large ranges of internuclear separation. Finally the project lead also to the first identification of an ion induced chemical reaction.

9. SIGNATURE OF PRINCIPAL INVESTIGATOR/ PROJECT DIRECTOR	TYPED OR PRINTED NAME	DATE
E. W. Thomas	Edward W. Thomas	10/5/77

NSF Form 98A (5-76)

Attachment to Form 98A (Grant DMR 73 02317)

List of Publications

1. "Ionoluminescence of Aℓ, Cu, and Mo; Optical Properties of Aluminum". M. Zivitz and E. W. Thomas. Phys. Rev. B 13, 2747 (1976).

2. "Ionoluminescence of Aluminum". M. Zivitz and E. W. Thomas. Proceedings of the 6th International Conference on Atomic Collisions in Solids, Amsterdam, Sept. 1975. Nucl. Inst. and Meth., 132, 411 (1976).

3. "Luminescence Induced by Ion Impact on Alkali Halide Crystals at High Temperatures (-160°C to 200°C). A. I. Bazhin, E. O. Rausch and E. W. Thomas. Phys. Rev. B 14, 2583 (1976).

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6. "Ion Induced Photon Emission From Solids. E. W. Thomas. "Proceedings of the 7th International Conference on Atomic Collisions in Solids." Moscow University Publishing House, Moscow 1977).

7. "Optical Emission from Low Energy Ion Surface Collisions." Chapter in "Inelastic Ion Atom Collisions" (Academic Press, N.Y. 1977, N. H. Tolk, Editor).